Agricultural Research Institute

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THE

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EDITED BY

*JAMES H. GARDINER, F.C.S.*

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# THE CHEMICAL NEWS.

VOLUME CXXII.

*EDITED BY JAMES H. GARDINER, F.C.S.*

No. 3169.—JANUARY 7, 1921.

## EDITORIAL.

ONE of the many revelations of the war has been that of our complete dependence upon Central Europe for the glass apparatus needed in the laboratory. As soon as the situation was realised our manufacturers set to work, and with patriotic determination took great risks in laying down expensive plant, erecting machinery to meet the demand of the moment, and to make a serious endeavour to retain in our own country this exceedingly important Key Industry. One phase of the War has passed now, and the second—the conflict of industry—has begun, and it is becoming increasingly evident that it needs more than the money and enterprise of the manufacturers to win through. The glass industry called for chemists and obtained them, and in many glass-houses the old traditional mixtures and working methods have given place to standard formulæ and scientific treatment.

One very serious thing, however, is lacking, and that is skilled workmen. The old hands are insufficient to do the extra work, and unfortunately the trend of events during the last five-and-twenty years or so has been such that young labour has gone off into directions needing less application.

The new educational conditions call for a new method of training, and the fact that the boy of to-day is better educated both in mind and body than was the working boy of twenty years ago should make it possible, by a sound method of intensive teaching, to produce the necessary skilled labour in a very short time.

Much good work is being done for the glass industry by the Society of Glass Technology, the Glass Research Association, and other similar bodies, but we think that the first individual effort to gain skilled workmen is being made by one of the oldest of our London glassworks, of which we give an account below.

## A NEW DEPARTURE IN THE GLASS INDUSTRY.

On Monday last, Mr. J. H. GARDINER, F.Inst.P., F.C.S., representing Messrs. James Powell & Sons (Whitefriars), Ltd., in company with Mr. P. Annett, Divisional Organising Officer for the Middlesex Educational Council, made a visit to Greenhill Drill Hall, and Harrow Weald Council Schools, and addressed the boys who, having reached the age of 14, were upon the point of leaving school. The object was to interest the boys in the glass industry, and to suggest to them the fine possibilities of good employment in the glass works that are now being erected at Wealdstone.

The Directors of the works, realising the serious lack of workmen to carry on the glass industry, have attacked the problem in a new and bold manner. The work carried on by the firm demands the highest possible skill, for they deal exclusively with high-class hand-made glassware. The present educational system keeps the boys at school until they are of such an age that it is hard to persuade them to go through the years of training that has hitherto been demanded to produce a skilled worker. The firm has, therefore, decided, with the assistance of the educational authorities, to attempt a system of intensive training. The scheme, which is due to Mr. J. H. Gardiner—who was for many years associated with the late Sir. W. Crookes—and whose skill in glass manufacture and manipulation is considerable, is in brief as follows.

The boys having been told the character of the work and the prospects that it holds out to them to learn one of the most important trades in the country, are invited to attend a series of evening continuation classes during the coming winter, a syllabus having been arranged to give a thorough grounding in English, arithmetic, the metric system, physical manipulation (woodwork, &c.), freehand drawing, and elementary chemistry and,

physics. After attending the classes a selection will be made of the most promising boys, who will then pass through a special course of technical lectures in glass, its chemistry and properties. After this they will be drafted into the works, where a special laboratory is being fitted up in which they, for a certain number of hours a day, will learn the rudiments of the many branches of the industry. The remaining portion of the day they will be employed in making themselves useful in one or other of the many departments of the firm. During this time of probation and instruction they will receive a small nominal wage, and as soon as, by their skill and industry, they are able to do useful work they will be passed into the works proper, and be paid the union wages for the duties they are fitted for. The speed at which they will learn their business will depend upon their own efforts aided by all the assistance that can be given to them in the way of instruction.

## THE FUNDAMENTAL CONSTANTS OF NATURE.

By HAWKSWORTH COLLINS.

IF the atomic weights of two elements be divided by their respective specific gravities it is recognised that the quotients give the relative volumes occupied by single atoms of those elements.

If the molecular weight of a pure chemical compound be divided by its specific gravity, it is recognised that the quotient gives the sum of the relative volumes of the atoms which form that substance, i.e.,

$$\frac{\text{Molecular weight}}{\text{Density}} = \text{Molecular volume or } \frac{m}{d} = v.$$

The molecular refractivity of a pure compound is obtained from the formula:—

$$\frac{n^2-1}{n^2+2} \cdot \frac{m}{d} = \frac{n^2-1}{n^2+2} \cdot v$$

where $n$ is the index of refraction.

The molecular magnetic rotation (M) of a pure compound is given by the formula:—

$$M = \frac{\alpha . m}{d} = \alpha\, v$$

where $\alpha$ is the magnetic rotation.

It is evident that the last two sets of constants are dependent upon the first set, viz., the molecular volumes.

It has been discovered that the relative volumes (when correctly found) of the elements reveal the constitution and structure of atoms in a definite manner. An example of this was given in the CHEMICAL NEWS, July 18, 1919.

It has also been discovered that the constants obtained from the heat of combustion are dependent in a particular manner upon the relative volumes of the elements.

Therefore, *the Relative Volumes of the Elements are the Fundamental Constants of Nature.*

These constants are invariable only at a constant temperature, so that it is necessary to choose a definite temperature. The ordinary one of 15° C. is most convenient as the great majority of experimental data are given at about that temperature and at ordinary atmospheric pressure. Since so much depends upon the relative volumes of atoms and molecules it is necessary to obtain these constants correctly.

No one can assert that both Perkin's and Bruhl's results with regard to Allyl bromide, *e.g.*, in Magnetic Rotation and Refractivity respectively are correct, for the former employed

Specific gravity 1·42532 at 15°
1·41057 at 25°
and the latter 1·3080 at 20°

There is a difference of about 1·5 per cent. in the two cases, and therefore the same percentage difference in the relative volumes. In other cases there is frequently a difference in their specific gravities of about 1 per cent.

Many scientists seem to think that Kopp solved the problem of relative volume, and that other people have slightly improved upon it; so it is necessary to go into the matter here, though as shortly as possible.

Kopp started by finding the relative volume of $CH_2$ at 0° C. to be 15·8. He then subtracted six times $CH_2$ from the total volume of hexane and found that the remaining two atoms of H together had a volume of about 30. He thought he had come to an absurdity, so he transferred his operations to the boiling points.

Dr. Cohen in his "Organic Chemistry," published in 1913, says: "The value of $CH_2$ can be determined by a comparison of different homologous series. The following table gives the constants for different classes of compounds at the boiling point and also the maximum and minimum values observed:—

| Series. | No. of Intervals. | Max & Min | Mean |
|---|---|---|---|
| Alcohols ... ... | 8 | 10·7—22·4 | 21·1 |
| Fatty Acids ... ... | 8 | 21·6—23·4 | 22·4 |
| Aldehydes (aliph.) | 4 | 10·0—22·0 | 20·7 |
| Amines (aliph.) ... | 5 | 20·4—20·6 | 20·5 |
| Alkyl iodides ... | 10 | 21·1—24·3 | 22·6 |
| Paraffins ... ... | 13 | — | 22·7 |
| Esters ... ... ... | 15 | 21·2—27·7 | 24·4 |
| Ethers ... ... ... | 13 | 21·6—28·5 | 24·3 |
| Hydrocarbons (arom.) | 5 | 21·0—22·0 | 22·1 |
| Olefines ... ... | 5 | 20·3—23·1 | 21·8 |

It will be seen that there is not only a considerable variation in the constants in the different series, but a wide divergence in the minima and maxima for the same series. It should, however, be pointed out that as a rule the value for $CH_2$ increases in ascending the series, and the longer the series and the wider the range of boiling points the larger the variation. There is clearly some missing factor which should be introduced to bring the various constants into uniformity."

These, then, are the data upon which Kopp founded his "discovery" that—the relative volume of $CH_2$ is *about* 22 at the boiling points of all substances containing it. And yet Dr. Cohen says: "With a delicate balance it is possible to estimate specific gravities with accuracy to one part in 100,000, and, as this is the principal factor involved in the determination of molecular volumes, the method experimentally leaves little to be desired." He then sums up all the attempts at the solution of this problem in the following words: "As no constant values can be attached to carbon, hydrogen and oxygen, it seems useless

to attempt to derive a molecular volume by the summation of atomic volumes."

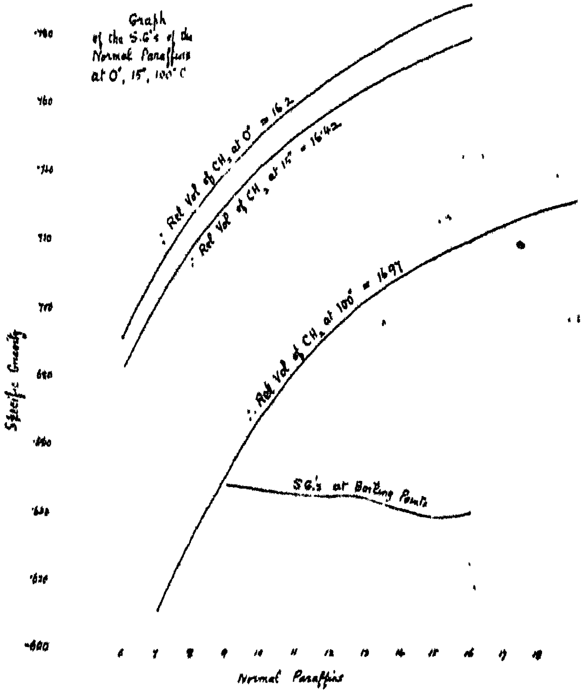
Dr. Cohen continues: "When Kopp's values for C, H, and O were calculated for compounds of the formula $C_aH_bO_c$ it was seen that the molecular volumes did not invariably conform to the calculated values and the property was therefore not strictly additive." Then he says: "Kopp showed subsequently that the calculated value would correspond with the observed result if account were taken of the oxygen atom . . . . The value for doubly linked oxygen was found a little higher that that for one atom of carbon . . . On this new basis the calculated values for forty-five different compounds did not vary by more than 4 per cent."

Now suppose there are two substances, A and B, which are similar in all respects, except that A has 5 methylene groups in its constitution and B 6; and suppose A boils at 120° C. and B at 150° C. At 120° the volume of $CH_2$ in each substance will be the same, and as B rises to its boiling point, the volume of each $CH_2$ is increasing. Therefore the volumes of $CH_2$ in the two substances are different at their boiling points.

Therefore it is impossible to compare the volumes of substances at their boiling points.

*Explanation of the Graph.*

The numbers 6-18 at the bottom of the graph represent the normal paraffins; *e.g.*, 9 stands for $C_9H_{20}$, 12 for $C_{12}H_{26}$ and so on. The numbers




0·600-0·790 written vertically represent specific gravities.

Forty-five out of several hundred, and correct within four per cent! If chemists are satisfied with this, of course it is no use discussing the matter further.

Fortunately for Kopp, Maxwell and Clausius discovered that—at their respective boiling points and at atmospheric pressure the molecules of various liquids occupy a space very nearly 0·3 times the total apparent volume. So they decided that he was right in taking the various boiling points as the stepping-stones from which to make his discovery. So it is necessary here to produce a proof that it is impossible to compare the relative volumes of substances at their boiling points.

Kopp found that at 0° C. the volume of $CH_2$ in all substances is 15·8. The correct value is 16·2.

At 15° C. it will be shown later that the volume of $CH_2$ in hundreds of substances is always 16·42.

At 100° C. it is 16·97 (see graph).

And at any other arbitrary temperature the volume is constant, gradually increasing with the temperature.

The three regular curves represent the graphs of the specific gravities of the paraffins at temperatures 0° C., 15° C., and 100° C.

If any point be chosen on the curve for 0°, say where the specific gravity of $C_7H_{16}$ is 0·712, and if the molecular weight (100) be divided by 0·712, the result (140·45) is the relative volume of the molecule $C_7H_{16}$ at 0° C.

If another point be taken on the same curve, say, where the specific gravity of $C_{14}H_{30}$ is 0·780, the relative volume is 253·85.

Subtract 140·45 from 253·85 and divide the result by 7 because there is a difference of 7 times $CH_2$ in the two molecules, the quotient is 16·2, which is the relative volume of the group $CH_2$ at 0°. Similar results will be obtained by taking any two points on the other two curves.

Now it is quite plain from these three curves that the graphs at any other arbitrary temperatures, say, 50°, 150°, and 200°, would be similar curves drawn in similar directions, and moreover

| | 0° | 15° | 100° |
|---|---|---|---|
| $C_6H_{14}$ ... ... ... ... | 0·691 | 0·6825 | |
| | 0·689 Warren | 0·678 15°·5 Schorlr | |
| | 0·695 Bartoli | 0.6985 14° Lachowicz | |
| $C_7H_{16}$ ... ... ... ... | 0·712 | 0·7022 | 0·610 |
| | 0·7085 Warren | 0·7023 14° Lachowicz | 0·616 90° Thorpe |
| $C_8H_{18}$ ... ... ... ... | 0·727 | 0·7177 | |
| | 0·719 Thorpe | 0·719 17°·5 Schorlr | |
| | 0·728 Wurtz | 0·7165 15°·6 Thorpe | |
| $C_9H_{20}$ ... ... ... ... | 0·740 | 0·7304 | 0·653 |
| | 0·733 Krafft | 0·731 16° Lemoine | 0·654 99° Krafft |
| | 0·743 Lemoine | 0·7330 0° Le Bas | |
| $C_{10}H_{22}$ ... ... ... ... | 0·751 | 0·7408 | 0·668 |
| | 0·7456 Krafft | 0·7324 20° Lachowicz | 0·669 99° Krafft |
| | 0·764 Lachowicz | 0·753 16° Lemoine | |
| $C_{11}H_{24}$ ... ... ... ... | 0·759 | 0·7497 | 0·682 |
| | 0·7560 Krafft | 0·7448 15° Krafft | 0·6816 99° Krafft |
| | 0·7816 Bartoli | 0·7581 20° V.N. | |
| $C_{12}H_{26}$ ... ... ... ... | 0·767 | 0·7572 | 0·693 |
| | 0·7655 Krafft | 0·7548 15° Krafft | 0·693 99° Krafft |
| | | 0·7684 20° V.N. | |
| $C_{13}H_{28}$ ... ... ... ... | 0·774 | 0·7637 | 0·702 |
| | 0·7716 Krafft | 0·7608 15° Krafft | 0·7008 99° Krafft |
| $C_{14}H_{30}$ ... ... ... ... | 0·780 | 0·7694 | 0·709 |
| | 0·775 5° Krafft | 0·7681 15° Krafft | 0·7087 99° Krafft |
| $C_{15}H_{32}$ ... ... ... ... | 0·784 | 0·7744 | 0·714 |
| | 0·776 10° Krafft | 0·7724 15° Krafft | 0·7136 99° Krafft |
| | 0·7724 15° Krafft | | |
| $C_{16}H_{34}$ ... ... ... ... | 0·788 | 0·7788 | 0·719 |
| | 0·7754 18° Krafft | 0·7754 18° Krafft | 0·7197 99° Krafft |
| | 0·7707 25° Krafft | 0·7707 25° Krafft | |
| $C_{17}H_{36}$ ... ... ... ... | | 0·7828 | 0·724 |
| | | 0·7764 22°·5 Krafft | 0·7[illegible]5 99° Krafft |
| | | 0·7714 30° Krafft | |
| $C_{18}H_{38}$ ... ... ... ... | | 0·7863 | 0·728 |
| | | 0·7768 28° Krafft | 0·7288 99° Krafft |
| $C_{19}H_{40}$ ... ... ... ... | | 0·7895 | 0·732 |
| | | 0·7774 32° Krafft | 0·7323 99° Krafft |
| | | 0·7720 40° Krafft | |

curves of this nature are the only ones which would give constant volumes for $CH_2$.

But the graph of the specific gravities at the boiling points (as shown) does not lie anywhere near the general direction of these curves, and therefore it is quite evident that the relative volume of $CH_2$ at the boiling-points is not anything like constant.

The table contains the experimental data, which are required for the graph.

There being no regularity in the relative volumes of substances at their various boiling points, if absolute regularity can be demonstrated to exist at a fixed temperature, of course the question as to which method of procedure is correct will be settled. And if this regularity produces an independent proof of the Constitution and Structure of the Chemical Elements as given in previous papers, the matter will be doubly settled; for the relative volumes, as supposed to have been obtained from the various boiling points, lead to absolutely nothing.

Again, if this regularity leads up to the demonstration of the Correlation of Physical Constants, such as those mentioned at the commencement of this paper, of course the matter will be trebly settled.

## A NEW INDICATOR.

By R. W. KINKEAD, B.Sc.

MOREAU (*Compt. Rend.*, 1901, cxxxii., 838) studied the effect of methyl nitrate on methyl magnesium iodide, which resulted in dimethyl-hydroxylamine; and Sand and Singer (*Ann.*, 1903, cccxxix., 190) state that nitric oxide and alkyl-magnesium bromides result in nitroso alkyl-hydroxylamine, but no work appears to have been done on the effect of aromatic grignard reagents on the $ONO_2$ group.

By the action of ethyl nitrate on phenyl magnesium bromide a deep blue solution was obtained which has the properties of an indicator, turning pink with acids and blue with alkalies.

One equivalent of ethyl nitrate $C_2H_5ONO_2$ was added gradually to one equivalent of $C_6H_5MgBr$, cooled in ice. In a few minutes a vigorous reaction takes place, with the evolution of heat. After standing over night, pieces of ice were added and the mixture left for a few hours for the magnesium compounds to settle. The etheral layer was then separated and the ether evaporated off. Solid $Na_2CO_3$ and water were then added,

when the mixture turned blue (later work shows that the colour is sometimes not developed till later). The mixture was then extracted with chloroform, when it was found that the blue colour remained in the aqueous layer.

This blue solution, which is obviously the sodium salt of the indicator, cannot be kept very long except as a very dilute solution. It was found that the best way to keep the substance was as an ethereal solution of the free indicator, so the blue solution was acidified, and the free red indicator extracted with ether.

The presence of chloroform seems necessary for the formation of the blue salt; all attempts to obtain the substance by extraction with ether resulting in compounds of the nitrolic acid type.

Like phenol phthalein, the substance cannot be used as an indicator in the presence of $CO_2$. In the absence of $CO_2$, very good results were obtained on testing the sensitiveness against phenol phthalein.

An N/10 solution of $H_2SO_4$ was titrated with an approximately N/10 solution of NaOH, using phenol phthalein and the new indicator.

Phenol phthalein :—

21·45 cc. NaOH solution neutralised 25 cc. N/10 $H_2SO_4$.

New indicator :—

21·5 cc. NaOH solution neutralised 25 cc. N/10 $H_2SO_4$.

The end point with the new indicator is very sharp and easy to observe, the last drop of acid or alkali making a radical change in colour. Three titrations did not differ from each other by more than 0·05 cc.

The substance is, unfortunately, not very stable, losing its colour and indicating properties on keeping. On concentrating a water solution of either the free indicator or the sodium salt, the substance also loses its colour and properties. On allowing an ethereal solution of the free indicator to evaporate, a few drops of a dark red liquid were obtained, which soon decomposed.

Both the free indicator and the sodium salt are very easily reduced by $SO_2$, but $H_2O_2$ seems to have no effect.

The depth of the colour indicates that the substance is of high molecular weight. Evidently there is some fundamental change during the reaction, as the ordinary course of a Grignard reaction will not give a final substance which shows the necessary tautomerism to account for the indicating properties, *i.e.,* from theory we would expect :—

$$C_2H_5ON{\genfrac{}{}{0pt}{}{//O}{\backslash O}} + C_6H_5MgBr \rightarrow$$

$$C_2H_5ON{\genfrac{}{}{0pt}{}{\genfrac{}{}{0pt}{}{//O}{-OMgBr}}{\backslash C_6H_5}} \xrightarrow{H_2O} C_2H_5ON{\genfrac{}{}{0pt}{}{\genfrac{}{}{0pt}{}{//O}{-OH}}{\backslash C_6H_5}}$$

which will not give the quininoid-benzenoid change of indicators.

Further work will be carried out to find the constitution.

Sir Donald Currie Laboratories,
Queen's University, Belfast.

## BRACKEN RHIZOMES AND THEIR FOOD VALUE.

By Prof. JAMES HENDRICK, B.Sc., F.I.C., University of Aberdeen.

(Concluded from vol. cxxi, p. 322.)

IN certain respects bracken rhizomes resemble potatoes in composition. In Table I. some average figures for potatoes are quoted from the recently issued Report of the Food (War) Committee, Royal Society (Report on the Composition of Potatoes grown in the United Kingdom. Food (War) Committee, Royal Society, 1919). The figures for "Arran Chief" are given as those of a potato of good quality, above the average in dry matter and in nitrogen. As compared with the potato-tuber, the bracken rhizome contains more dry matter, but the dry matter is not quite so high in soluble carbohydrates, and is much more fibrous. In albuminoids it has already been seen that bracken rhizomes vary greatly. Potatoes are not so high in this valuable constituent as the B samples from Craibstone, but are higher than the A samples and than the samples in Table I.

In the case of the potato the main part of the solid matter consists of starch, which forms most of what is called "soluble carbohydrates." Bracken rhizomes also contain starch in considerable quantity, but, unlike the potato, the larger part of the soluble carbohydrates does not consist of starch, but of other substances of an undetermined nature.

In order to test whether animals would eat bracken rhizomes, and if so whether they would thrive upon them, a number of feeding trials were made with different classes of stock. It had already been reported from various sources that pigs will root up and eat bracken rhizomes, and it is recorded that these have been used in Europe as human food in times of scarcity. It is also on record that they formed a portion of the food of the natives of New Zealand at the time of the discovery of that country by Captain Cook. Attempts were made in our experiments to feed these rhizomes to pigs, to cattle, and to poultry.

On account of the many difficulties of the times it was almost impossible to arrange accurate feeding trials in 1918. Many people were suffering from lack of food stuffs, and were quite ready to give any promising new substance a trial, but very few had the necessary time and labour for weighing out foods and weighing stock, and otherwise giving the attention required for carrying out a reliable feeding experiment.

Some rough trials were first made, and these showed that at any rate bracken rhizomes were not very palatable to stock. Pigs would not eat them if they were already accustomed to a liberal diet, especially of concentrated foods. They took them only when they were in lean condition and, generally speaking, breeding stock consumed them more readily than feeding stock. It was also discovered that pigs ate them more readily if the rhizomes were given to them in the rough state, just as they were dug from the soil. It was at first assumed that if they were cleaned, chopped, mixed with other food, and cooked, the animals would consume them more readily. This proved to be quite wrong. Whether mixed with other

foods or not, pigs liked them better uncooked and unwashed.

The rhizomes were also tried in the form of meal. A few tons were dried in a malt kiln, after which it was found that they could be readily ground to meal. Indeed they could be ground too readily, for the workmen who carried out the milling raised serious objections to the work on account of its excessive dustiness. The meal so obtained was found to have the following composition:—

| | Per cent |
|---|---|
| Moisture | 9·81 |
| Ether extract (oil, &c.) | 2·54 |
| *Albuminoids | 9·56 |
| Soluble carbohydrates | 41·26 |
| Fibre | 20·49 |
| †Ash | 16·34 |
| | 100·00 |
| * Containing total nitrogen | 1·53 |
| Containing protein nitrogen | 1·49 |
| † Containing siliceous matter (sand, &c). | 11·26 |

The rhizomes which were dried were dug in May, when considerable growth of frond had already taken place, and they were not therefore of such good composition as if they had been dug a month earlier. It was found impossible, in view of the labour conditions then prevailing, to have them washed. This accounts for the high percentage of ash and sand which they contained.

Some feeding experiments with pigs and poultry were carried out with the help of members of the staff of the West of Scotland College of Agriculture, and the results are detailed in *Bulletin* No. 89 of the College, "Report on Experiments of the Feeding Value of Bracken Rhizomes for Pigs and Poultry." Preliminary trials were made at Holmes Farm, Kilmarnock, in which it was shown that breeding sows would eat considerable quantities of the rhizomes without any evil effect, but that well-fed feeding animals could not readily be induced to eat them. Then, through the kindness of the Directors of the Scottish Co-operative Wholesale Society, and of Mr. Geo. C. Young, their manager, a more accurate test was made on two pens of pigs at Calderwood Estate, East Kilbride, under the supervision of Mr. James Wyllie, B.Sc., of the West of Scotland College. These pigs had been somewhat short of food, and as their appetites were not pampered, they ate their allowance of bracken, whether in the form of untreated rhizomes or ground into meal, with apparent relish. But the results of the experiment were unsatisfactory, as the pen of pigs which got bracken in addition to the foods given to the other pen showed very little benefit from the extra food. The pigs which got bracken made a live-weight increase of 0·77lb. per head per day over a period of 140 days, while those without it made an increase of 0·71lb. per head per day. The small increases made all over were due to the poor diet on which the pigs were kept owing to the scarcity of feeding-stuffs, but the pen which had from 1lb. up to 2lb. of bracken meal per head per day as an addition to their ordinary diet did very little better than the others.

Mr. James Picken, Milton, Kircudbright, also tried both the untreated bracken and the meal with pigs, but was not in a position to do any weighing. He reported, however, that the pigs ate the bracken "with evident relish," and that it could "well replace other fresh vegetable food during the winter and spring months." Mr. Picken also noted that the bracken appeared to make the pigs lively, and that those which received it took more exercise than the others. He remarks: "This is a decided advantage to pigs 6 weeks to 4 months old, but over that age and during the fattening period it might be necessary to withold the roots, as these might unnecessarily excite the pigs and thus delay the fattening process."

The evidence, so far as it goes, indicates that bracken rhizomes in the fresh state or as meal might be of some use as a maintenance food for pigs, but are not of much use as a fattening food.

With poultry the results were still less favourable. The experiments were carried out with bracken meal at the Poultry Department, Holmes Farm, Kilmarnock, by Miss Agnes Kinross of the West of Scotland Agricultural College. The birds did not like the bracken meal even when it was mixed with a considerable amount of other food, and the pen which received a little bracken in their food during October and November did not lay so well as others which had received no bracken meal but an equivalent in other foods. The experiment indicates that bracken meal is not a suitable food for egg-production.

Bracken meal was tried with feeding cattle at Craibstone, the experimental farm of the North of Scotland Agricultural College of Agricutlure. The quantity available was not sufficient for an experiment on a scale large enough to be satisfactory, as for that purpose 8 or 10 bullocks would require to have been fed with the meal for a period of several weeks, and the quantity should gradually have been raised to several pounds per head per day. The quantity available was only sufficient to enable two bullocks to get 1lb. per head per day for two months. A comparison lot of two bullocks was similarly fed, but without bracken meal.

Lot 1 (bracken meal) received daily 95lb. turnips with oat straw *ad lib.*, and 2lb. bruised oats, 2lb. cereal offals, and 1lb. bracken meal.

Lot 2 received daily the same amount of turnips and straw and 2½lb. each of bruised oats and cereal offals.

Lot 2 therefore received ½lb. oats and ½lb. cereal offals instead of 1lb. bracken meal given to Lot 1.

Both animals in Lot 1 ate the bracken meal with evident relish, and they would have taken more had we been able to supply it. The increases made by the two lots were somewhat similar. In 56 days the cattle in Lot 1 made an average increase of 132lb., or 2·4lb. per head per day, while those in Lot 2 made an average increase of 113lb., or 2·0lb. per head per day. The lot which got the bracken meal therefore did slightly better than the other, but no weight can be attached to this result, as the number of animals under experiment was too small, and the amount of bracken meal fed was only a small proportion of the whole food. So far as it goes, however, the experiment shows

that feeding bullocks will readily eat a moderate amount of bracken meal, and that it appears to agree quite well with them.

It cannot be claimed that the feeding trials made with bracken rhizomes are anything more than preliminary. If the food value of this substance is to be tested thoroughly, much larger and more exhaustive trials will be necessary, and far larger quantities of the rhizomes would require to be obtained for the purpose. So far as they go, however, the trials indicate, as the analysis also does, that bracken rhizomes are not rich enough in the more valuable food constituents, such as albuminoids, to be of much use for anything but maintenance purposes, and that even for such purposes their usefulness is limited by the fact that they are not very palatable to certain classes of stock. Fortunately the circumstances which gave rise to these experiments have now passed away, and there is no longer the same danger of acute food scarcity in this country. In clearing from the bracken pest land which is good enough for cultivation, it may be possible to utilise the crop of rhizomes for feeding purposes, and these experiments indicate the value of this substance as a food and its limitations. They may also be of some interest in showing that the best time to cut bracken in order to weaken the rhizome is just when the frond is fully expanded.—*Transactions of the Highland and Agricultural Society of Scotland*, 1919.

## CHEMICAL NOMENCLATURE AND PRONUNCIATION.

By J. NORMAN TAYLOR,
Washington Preparatory School, Y.M.C.A., Washington, D. C.

THE attention of educators is frequently called to the responsibility of secondary schools in the matter of preparing students for institutions of higher learning. Slow progress in college is attributed to lack of proper training in the student's preparatory life and not infrequently, failure in later life is ascribed to faults of secondary schools. A well-known research director, in writing of the lack of observation among chemists, states that "until a conscious effort is made in our primary education to meet this requirement, our advance in science will not be as speedy as it should" (Robert E. Rose, "The Education of the Research Chemist": *Jour. Ind. and Eng. Chem.*, 1920, xii., 948). A prominent educator implies this same lack of adequate preparation when he says, "And even if a freshman is somewhat dulled by his previous training, that seems scarcely a good reason for going on with the dulling process" (C. G. MacArthur: "The Scientific Teaching of Science": *Science*, new ser., 1920, lii., 350). Not only as regards preparation in science is deficiency laid at the door of the secondary school, but the poor English employed by so many college graduates is likewise charged to the same source. "A university graduate's inaptitude in the art of writing may be due, however, not to faults in his university course; more likely it is due in part to inefficient methods employed in the schools in which he obtained his earlier training in English" (George McLane Wood: "Suggestions to Authors": *U.S. Geological Survey*, 1916, p. 52).

Granting the fact that the lower schools are responsible for deficiencies which handicap the individual later on, it will be agreed that in secondary schools, method is of great importance. If we are to utilise the scientific method in teaching science, then it follows that in English-speaking countries good English, both with regard to spelling and pronunciation, should be used to convey our thoughts regarding science.

Although, perhaps, not a vital matter, it nevertheless appears to the writer that in teaching chemistry, the nomenclature used in secondary schools, so far as chemical words and terms are concerned, should agree with that employed in the higher institutions of learning. Dean Wilbur in speaking of good use in language, with particular reference to national use, says, "There is a law of national use that restricts us to those words that are in good use throughout the land . . . . A word that is not in good current use throughout the land is inefficient. Misunderstanding and perplexity and vagueness follow in the track of such a word" (William Allen Wilbur, "English Rhetoric": Judd and Detweiler, Inc., Washington, 1917, p. 260). In instances where chemical facts have been conveyed to the preparatory school student through the medium of corrupt English, confusion is bound to follow when his teacher in college uses pure English. And a change from pure English to corrupt forms is equally confusing. Certainly, there should not be any confusion in this regard and greater uniformity should obtain both as to terminology and pronunciation.

If it is correct to spell the word phosphorous with "ph," why should not the same principle in orthography be followed when writing the word sulphur? Good English would require that the names of the members of the halogen group be spelled with the final "e," as "fluorine," "chlorine," "bromine," and "iodine," and that they be pronounced as they are spelled and not as though the termination were "in." Likewise good English demands that the names of the chemical compounds known as the halides be spelled with the final "e" and that they be pronounced as they are spelled (consult "Inorganic Nomenclature" in the introduction to a "German-English Dictionary for Chemists," by Austin M. Patterson, published by John Wiley & Sons, Inc., New York, 1917). The names of analogous compounds should terminate in "ide," as for example: carbide, oxide, sulphide, phosphide, nitride, selenide. The names of these compounds should not be pronounced as though they terminated in "id." Acids, bases, and salts should be written and pronounced with a proper regard for good English (examples of good chemical nomenclature are to be found in "A Dictionary of Chemical Terms," by James F. Couch, published by D. VanNostrand Co., New York, 1920). In naming salts, the negative terminations should be "ate" and "ite" and the names should be pronounced as they are spelled and not as though they terminated in "at" and "it".

We must conclude with Dr. Crane that "good English in chemical literature, particularly in naming compounds, needs cultivation" (E. J. Crane, "Chemical Nomenclature": *Jour. Ind. and Eng. Chem.*, 1919, xi., 72). Its choice is based

on a proper regard for derivation and good usage, and this latter desideratum requires the use of pure Englsh by English-speaking people, both in writing and pronunciation. Elimination of un-English terminology in chemical literature may be brought about by following Dean Wilbur's injunction: "Cultivate your own heritage. Cast away your mannerisms and discard your provincialisms, but cherish as a trust your own style and express it in our common language for the common good." Let those who teach chemistry in our schools and colleges observe good usage and adhere strictly to real English rather than to individual preferences.—*School of Science and Mathematics*, U.S.A., December, 1920.

## NEW METHOD FOR MANUFACTURE OF NITROGENOUS FERTILISERS.

AN interesting paper on this subject was read by Mr. Thorsell, engineer, at a meeting of the Association of Engineers of Gothenburg, relating to a new method for preparation of nitrogenous compounds.

The method has many points of resemblance with the Haber process, but is more economic and more reliable in practice. It has also the advantage of giving useful by-products such as formiates oxalates, &c. Gaseous cyanogen is prepared by electrolysis of cyanides and the gas thus produced is run through concentrated hydrochloric acid, where it is transformed into oxamine, which represents a remarkable nitrogenous fertiliser containing 30 per cent nitrogen. Owing to the high cost of coal, heating is effected by electricity, and the expenditure of energy could thus be reduced to such an extent that only 12 kilowatts are needed to manufacture one kilogrm. of combined nitrogen.

Manufacture has already been commenced at the works of the Kvaeveindustrie Co., but as yet one cannot estimate the yield, for hitherto only a small portion of the plant is in work owing to the want of power. However, before long the fertiliser may be in the markets. The products comprise a series of by-products. To what extent will this new fertiliser compete with the hydro-electric nitrate of Norway? This, of course, will depend upon its value and price.—*L'Engrais*, November 19, 1920.

## SIMULTANEOUS UTILISATION OF PYRITES CINDERS AND BISULPHATES FOR MANUFACTURE OF IMPURE FERRIC SULPHATE.

COAGULATION of blood in abattoirs, deodorisation of putrid meat, waste fish, &c., require large quantities of ferric sulphate.

Consequently it is useful to manufacture this material cheaply by the action of residual pyrites on cinders (two substances of no appreciable value).

$$6SO_4NaH+Fe_2O_3=\underset{\text{Utilisable mixed salt}}{\underline{(SO_4)_3F_2+3SO_4Na_2+3H_2O}}$$

These experiments, made in the Iodet Angibaud Works of La Rochelle, might be continued for some time longer so as to be absolutely sure of the identity of this method with the old ones.

In any case, says M. Hutin (*Revue de Chemie Industrielle*, November, 1920), we have to thank Messrs. Iodet Angibaud for allowing us to make the following tests:—

Pure pyrites cinders 40 kilogrms. require 180 of $SO_4NaH$, supposed to be pure (40·8 per cent $SO_4H_2$ free) and give 100 of $(SO_4)_3H_2$ (mixed with variable quantities of $SO_4Na$).

This ferric sulphate can be manufactured at a cost of less than 5 francs per quintal (4s. per 220½lbs.). The exact quantity of pyrites and bisulphate to be added is calculated according to the cinders with an exact percentage of $Fe_2O_3$ and the real acidity of the bisulphate in $SO_4H_2$.

*Modus Operandi.*

The bisulphate is only slightly heated and then the dry cinders added in small quantities while stirring briskly. The reaction is very violent. The bisulphate pans are only filled 2/5. Heating is continued to remove water. The material run off should be very dry. To coagulate blood ¼-part of this magma ¾ of blood. Coagulation is good cold, but the experimenter is of opinion that it would be better to heat. These experiments might be continued.

## CORRESPONDENCE.

### IS H COMPOSED OF A WHOLE-NUMBER PART (*A*) PLUS AN AUXILIARY PART (*B*) AND A ROTATING ELECTRON (*C*)?

*To the Editor of the Chemical News.*

SIR,—Referring to the above paper which appeared in your Journal of Dec. 31, 1920, through an oversight I omitted to mention that Langmuir gives helium the place shown in Table II. as well as the one over beryllium.

Referring to Table I., Co, Rh, and Ir should be deleted.

Referring to the descriptive matter under Table II., on p. 316, the letters "A" and "B" (in small caps.) should be in large caps. (A,B): the same as those following the words "Atomic Number."

There are two additional matters of interest I will note here.

If *a* is the fundamental material having the property of cohesion uniquely developed, it might condense round a nuclear part *b*, the latter possibly representing the *positive electron*, so that all atoms would contain at least one *b* nucleus, presumably situated at the centre of the atom. There are, however, apparently insuperable difficulties that stand in the way of such an idea. One of the difficulties would be the evaluation of the positive entity in different elements. Obviously, oxygen could not have more than one such entity if the *a*-value of unity is retained; and yet oxygen is supposed to have 8 negative electrons. There would thus be a very large excess of negative charge on (and in) the atom; equal to 7 negative electrons. Helium, for example, presents a similar difficulty.

The positions of $a$ and $b$ in the table shown might be reversed. Moreover, to make the table more complete, the negative electron should be placed therein; but it is obvious that it may be stretching matters too much to attempt to assign such an electrical entity to a place in the table.

It is of interest to note that A. G. Dempster reports in *Science* of December 10, 1920, that he has analysed magnesium by means of the positive-ray method, with the result that the atomic weights of the whole-number isotypes found are: 24, 25, and 26. Mg=24 is present in larger quantities than the others.—I am, &c.,

F. H. LORING.

## COLOUR OF WATER.

*To the Editor of the Chemical News.*

SIR,—Sir W. D. Bancroft, in a recent paper (CHEMICAL NEWS, 1919, cxviii., pp. 197, 208, 222, 233, 248, 254) has discussed the question of the colour of water, with regard to the theories that its colour under various conditions is due to absorption of light, reflection by suspended particles, influence of dissolved matter, &c., but he has overlooked the aspect of the question raised by Ducleaux and (Mme.) E. W. Wollemann (*Journ. de Physique*, 1912, (v.), ii., 263). These investigators found that a long column of water appears blue by transmitted light at comparatively low temperatures, but it becomes green with rise of temperature, which they explain on the assumption that polymerised water molecules are blue, and the simple ones green, the former being broken up with increasing temperature. Confirmation is afforded to this explanation by the fact that solutions of colourless salts, which must contain less polymerised water molecules than pure water, are greener than pure water at the same temperature.

Of course, the vapour density of steam is much less than that required for the formula $H_4O_2$, and greater than for the formula $H_2O$, its density at about 100° C. corresponding with about 91 per cent of $H_2O$ molecules, whilst more recent work has rendered it necessary to assume the existence of trihydrol ($H_6O_3$) in addition to dihydrol ($H_4O_2$) and hydrol ($H_2O$) in liquid water, in addition to which H. E. Armstrong assumed that two intra-molecular forms of each "hydrol" also exist.

If these assumptions be true, then the six different forms of ice discovered by G. Tammann (*Zeit. physical Chem.*, 1910 and 1912) correspond to the six different molecules assumed to exist in liquid water.—I am, &c.,

E. TOMKINSON.

Barrow-in-Furness, December 24, 1920.

## DIAMONDS.

*To the Editor of the Chemical News.*

SIR,—In the course of his paper on "Diamonds" (CHEMICAL NEWS, cxx., 303), Mr. J. R. Sutton mentions the breast-plate of the high priest at Jerusalem and raises the question as to whether one of the stones was a diamond, inclining to the belief that possibly it was. If, as Mr. Sutton suggests, the art of engraving on the diamond may have been known to the ancients, it is highly probable that some examples would have been preserved, but nothing of the kind has ever been found. While diamonds have occurred having natural markings simulating written characters, it is highly improbable that any of these would be sufficiently like the symbol of one of the tribes to pass muster, and in any case there is no evidence that the Jews had any knowledge of the diamond as a precious stone.

Moreover, not one breast-plate, but quite a number had to be constructed to replace those carried off by the Egyptian and Babylonian plunderers who devastated the Holy City at various dates from 971 B.C. The question was very fully discussed by Mr. L. Fletcher, Special Guide No. 5, British Museum (Nat. Hist.) 1911, who shows clearly that the name diamond given in the Bible is a mis-translation and that quite a different stone was involved.—I am, &c.,

THOMAS STEEL.

Sydney, N. S. Wales.

## THE BRITISH COMMITTEE FOR AIDING MEN OF LETTERS AND SCIENCE IN RUSSIA.

*To the Editor of the Chemical News.*

SIR,—We have recently been able to get some direct communication from men of science and men of letters in North Russia. Their condition is one of great privation and limitation. They share in the consequences of the almost compelte economic exhaustion of Russia; like most people in that country they are ill-clad, underfed, and short of such physical necessities as make life tolerable.

Nevertheless, a certain amount of scientific research and some literary work still goes on. The Bolsheviks were at first regardless and even in some cases hostile to these intellectual workers, but the Bolshevik government has apparently come to realise something of the importance of scientific and literary work to the community, and the remnant—for deaths among them have been very numerous—the remnant of these people, the flower of the mental life of Russia, has now gathered together into two special rationing organisations which ensure at least the bare necessities of life for them.

These organisations have their headquarters in two buildings known as the House of Science and the House of Literature and Art. Under the former we note such great names as those of Pavlov the physiologist and Nobel Prizeman, Karpinsky the geologist, Borodin the botanist, Belopolsky the astronomer, Tagantzev the criminologist, Oldenburg the orientalist and permanent secretary of the Petrograd Academy of Science, Koni, Radlov, Bechterev, Latishev, Morozov, and many others familiar to the whole scientific world.

Several of these scientific men have been interviewed and affairs discussed with them, particularly as to whether anything could be done to help them. There were many matters in which it would be possible to assist them but upon one

in particular, they laid stress. Their thought and work is greatly impeded by the fact that they have seen practically no European books or publications since the Revolution. This is an inconvenience amounting to real intellectual distress. In the hope that this condition may be relieved by an appeal to British scientific workers, Prof. Oldenburg formed a small committee and made a comprehensive list of books and publications needed by the intellectual community in Russia if it is to keep alive and abreast of the rest of the world.

It is, of course, necessary to be assured that any aid of this kind provided for literary and scientific men in Russia would reach its destination. The Bolshevik Government in Moscow, the Russian trade delegations in Reval and London, and our own authorities have therefore been consulted, and it would appear that there will be no obstacles to the transmission of this needed material to the House of Science and the House of Literature and Art. It can be got through by special facilities even under present conditions.

Many of the publications named in the Oldenburg list will have to be bought, the costs of transmission will be considerable, and accordingly the undersigned have formed themselves into a small committee for the collection and administration of a fund for the supply of scientific and literary publications, and possibly if the amount subscribed permits of it, of other necessities to these Russian savants and men of letters.

We hope to work in close association with the Royal Society and other leading learned societies in this matter. The British Science Guild has kindly granted the Committee permission to use its address.

We appeal for subscriptions and ask that cheques should be made out to the Treasurer, C. Hagberg Wright, LL.D., and sent to the British Committee for aiding Men of Letters and Science in Russia, British Science Guild Offices, 6, John Street, Adelphi, London, W.C.2.—We are &c.,

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| MONTAGU OF BEAULIEU | BERNARD PARES |
| ERNEST BARKER | ARTHUR SCHUSTER |
| E. P. CATHCART | C. S. SHERRINGTON |
| A. S. EDDINGTON | A. E. SHIPLEY |
| I. GOLLANCZ | H. G. WELLS |
| R. A. GREGORY | A. SMITH WOODWARD |
| P. CHALMERS MITCHELL | C. HAGBERG WRIGHT. |

## NOTICES OF BOOKS.

*Year Book of Pharmacy for* 1920. Pp. ix+622. London. J & A. Churchill, 7, Great Marlborough Street.

THIS Year Book of Pharmacy contains Abstracts of papers relating to pharmacy, materia medica, and chemistry contributed to British and foreign journals from July 1, 1919, to June 30, 1920, also it contains the Transactions of the British Pharmaceutical Conference at its 57th Annual Meeting held in Liverpool, July 19, to 23, 1920.

*The Yeasts.* By ALEXANDRE GUILLIERMOND, D.Sc., translated by F. W. TANNER, M.S., Ph.D. Pages xix.+424. 1920. London: Chapman & Hall, 11, Henrietta Street, W.C.2. Price 33/- net.

ALTHOUGH it is stated that Mr. Tanner is the translator of Mr. Guilliermond's book on Yeasts, this is not strictly correct. This book is based on Guilliermond's "Les Levures" which was published in 1912, appearing as a volume in the section on Cryptogramic Botany of Encyclopedic Scientifique. This series is edited under the direction of Dr. Toulouse. The mere translation of a book published in 1912 on a subject which is being developed as rapidly as the yeasts would be entirely inadequate, the translator has, with the assistance of M. Guilliermond, added much new material, which has been published since 1912.

The book is divided into 13 chapters. The first seven deal with the properties of yeasts, while the remaining chapters are given up to their classification.

*A System of Physical Chemistry.* Vol. II., "Thermodynamics." By WILLIAM C. McC. LEWIS, M.A. (R.U.I.), D.Sc. (Liver.). Third Edition. Pp. viii.+454. 1920. London: Longmans, Green, & Co., 39, Paternoster Row, E.C.4. Price 15/- net.

THIS book belongs to the series "Text Books of Physical Chemistry" edited by Sir Wm. Ramsay, K.C.B., D.Sc., F.R.S., and F. G. Donnan, C.B.E., M.A., Ph.D., F.R.S.

The author has made a few additions to the previous edition, principally in Chapter VII., the E.M.F. method of determining the transport number of an ion as employed by MacInnes and Parker, an account of the investigation of Richards and Daniells on thallium amalgam cells, and Tolman's work on centrifugal cells; in Chapter VIII., an extended section dealing with ionic activity and ionisation. The problem of the activity of undissociated molecules is also considered. In Chapter XI., a *resumé* of the experimental evidence for Donnan's theory of membrane equilibria is given, and a fairly full account of the concept of the micelle in electrolytic colloids.

The other two volumes comprising this book are entitled: Vol. I., "Kinetic Theory"; and Vol. III., "Quantum Theory."

*An Introduction to the Structure and Reproduction of Plants.* By FRITCH and SALISBURY. London: G. Bell & Sons. Price 15/- net.

AS stated by the authors, this work, of some 400 pages, is written as a sequel to their "Introduction to the Study of Plants." The subject-matter is divided into two sections, the first dealing with anatomy, and the second with life-histories and reproduction. Both these sections are copiously illustrated by photographs and diagrams, very largely original; these are extremely well reproduced and form a valuable part of the book.

In the anatomy section are chapters on cell-structure, cell-division, and differentiation, with separate chapters on the non-living contents and by-products of cells. These are followed by sections devoted to the different tissues in turn, special emphasis being laid on the relations of structure to function in special tissues such as cork, secondary wood, and the like.

In the second section, dealing with life-histories and reproduction, a departure has been made from the usual system of "types." The common groups are all dealt with in turn, but as large a variety

of forms as possible is illustrated in each. In accordance with this principle, many interesting references of economic and commercial importance are introduced. The short concluding chapter deals simply with evolution and heredity; its interest is increased by clear diagrams of simple laws of variation and maps illustrating distribution.

Finally, there is a comprehensive appendix and an excellent index. The microscopic diagrams would be improved by statements of the exact magnifications.

## NOTES.

Candelilla Wax in Mexico.—The candelilla is a plant about 25 inches high which grows extensively in Mexico, wild, especially in the locality of Monterey, where there are several works to extract the oil. At the end of August, 1919, only one of these works was running, owing to the poor prices of wax, the daily production being 662lb. The wax is extracted by putting the plants into water, which is then heated to boiling. Sulphuric acid is added, the separated wax being collected and poured into receptacles to solidify. It is then treated with steam in another vessel, and sulphuric acid. The refined wax is then run into moulds.—*Matières Grasses,* Nov. 15.

Mr. John Ames, General Secretary of the Industrial League and Council, has been appointed a member of the Commercial Panel of the Appointments Department of the Ministry of Labour. Mr. Ames' long and varied experience in connection with Labour matters renders him eminently suitable to assist in connection with the work which will devolve on this Panel. During the last two years, while officiating in the capacity of a Trustee and Member of the Executive Committee administering the King's Fund, of which Lord Parmoor was the Chairman, Mr. Ames found his experience very useful.

New Commercial Motor Taxation.—The Solicitor to the Commercial Motor Users Association has compiled for the benefit of members a 24-page booklet, indicating the new rates of duty payable upon commercial motor vehicles as from January 1, together with a summary of the principal regulations governing the licensing and registration of such vehicles, which will also come into force on January 1. A limited number of copies of the booklet are available, and any user of commercial motor vehicles may receive a copy post free upon application to F. G. Bristow, F.C.I.S., F.S.S., A.M.Inst.T., General Secretary, Commercial Motor Users Association, 50, Pall Mall, London, S.W.1.

Export of Seed Potatoes.—The Board of Trade (Licensing Section) announces that as from the 16th instant seed potatoes may be exported to all destinations other than Soviet Russia without Privy Council Licence. Exporters are, however, warned that it will still be necessary to obtain certificates of freedom from disease from the respective Boards of Agriculture before export can take place to certain destinations.

Contracts Closed.—The Turbine Furnace Co. Ltd., of 5, Budge Row, London, E.C.4 has received orders from (1) Messrs. A. Boakes Roberts & Co., Ltd., of Carpenters Road, Stratford, E. (chemical manufacturers) for one set of furnaces for a 30ft. by 8ft. Lancashire Boiler, with 3in. flues; (2) Messrs. The Gas Light & Coke Coke Co., Ltd., Westminster, have placed an order for one set of Turbine (Patent) Furnaces, for their tar and ammonia-producing works at Beckton. The furnaces are required to fit a Lancashire boiler of 8ft. 6in. diameter.

Estimation of Phosphates and Arseniates.—The sulphomolybdic solution hitherto employed to characterise, sometimes tin salts and sometimes hydrogen peroxide, gives an extremely sensitive reagent which M. Denigès employs in research of phosphates and arseniates. Its application will be particularly interesting in analysis of soils and identification of traces of Ph or As, both in biochemistry and legal chemistry.—*Comptes Rendus,* October 26th, 1920.

## New Patents.

This List is specially compiled for the *Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, W.C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

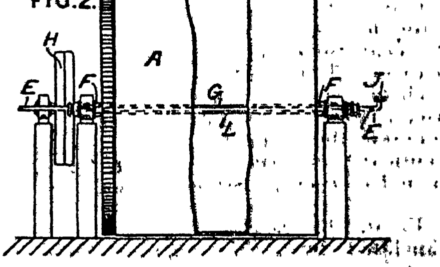
*Mixing or comminuting and dissolving alkali silicates.*—Mr. J. F. Phillips, of Old Burlington-Street, London, and another gentleman have obtained a Patent No. 151508, for an improved method of mixing or comminuting and dissolving alkali silicate in the presence of water under the action of steam or gas in a rotary mixer. The steam or gas is arranged to be directed in the form of jets throughout the whole internal space of the mixer and to impinge with force upon the particles of the material treated. Preferably, a pipe is arranged substantially along the axis of the barrel or cylinder and provided along its length with a number of orifices so as to cause radical jets of steam, etc., to play upon the material as it tumbles with the rotation of the barrel.

There may be a number of pipes substantially parallel to the axis; or the steam may be admitted to a steam-chest at one end or both ends of the cylinder provided with a series of perforations which will cause a number of jets to be projected into the cylinder parallel to the axis. As shown on the accompanied drawing the cylinder A, is mounted on trunnions F and rotated by toothed gearing, and a steam-pipe E passing through the trunnions is fitted at the end with a safety valve J. The pipe E has radical orifices L and may be surrounded by a second or shutter pipe G having orifices normally registering with those in the pipe E.

By means of a handle H, the pipe G can be rotated to close the orifices L of the pipe E, or the pipe G may be arranged to be moved axially. The pressure of the steam or gas in the cylinder may be employed to discharge the finished material.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and forward on post free for the official price of 1/- each.

FIG. 2.




### *Latest Patent Applications.*

35629 & 35630—British Cellulose & Chemical Manufacturing Co.—Treatment of products made with cellulose derivatives. Dec. 18th.

35647—British Dyestuffs Corporation.—Manufacture of new series of soluble acid colouring-matters, and of new series of intermediate compounds for manufacture thereof. Dec. 18th.

35196—Clavel, R.—Process of dyeing cellulose acetate. Dec. 14th.

35523—Scheibler, H.—Manufacture of sulphur preparations of the thiophene series. Dec. 17th.

*Specifications Published this Week.*

132510—Gans, R.—Process for the production of iron-free ammonium alum from aluminium sulphate solutions containing ferric sulphate.

135187—Aktiebolaget Ferrolegeringar.—Production of chromium or alloys of chromium.

147543—Traube, W.—Process for the extraction of ethylene from gaseous mixtures containing it.

*Abstract Published this Week.*

Particulars are just to hand of a simplified method of obtaining alkali percarbonates which has been patented by M. H. Wade, of Hatton Garden, London, No. 152368.

Solid alkali percarbonates are obtained by treating sodium carbonate with hydrogen peroxide in presence of sufficiently limited quantities of water to produce the solid product directly, and of sodium chloride for salting out the product. A previous calcination of the sodium carbonate, and the addition of anti-catalysers such as sodinm silicate, magnesium chloride and magnesium—sodium silicate are advantageous.

Messrs. Rayner & Co., will obtain printed copies of the published specification and will forward on post free for the sum of 1/- each.

## MEETINGS FOR THE WEEK.

*Saturday, January 8, 1921.*

Royal Institution, 3. (Christmas Lectures). "The Haunts of Life—The Conquest of the Land," by Prof. J. Arthur Thompson.

*Tuesday, January 11.*

Royal Institution, 3. "The Mastery of the Air," by Prof. J. Arthur Thompson.
Institution of Electrical Engineers, 7. (At Edinburgh).
Institute of Metals, 7.30. (At Birmingham).
Institute of Metals, 6. (At Glasgow).

*Wednesday, January 12.*

Royal Society of Arts, 8. "Industrial Fatigue," by Charles S. Myers, M.D., Sc.D., F.R.S. W. L. Hichens (Chairman, Messrs. Cammell Laird & Co., Ltd.) will preside.
Institute of Electrical Engineers, 7. (At Birmingham).

*Thursday, January 13.*

Institute of Chemistry. (At Liverpool).
Institution of Electrical Engineers, 6. "Electrons," by Sir W. H. Bragg.
Optical Society, 7.30.

If in good condition, Sixpence per copy will be paid for any of the undermentioned numbers of the CHEMICAL NEWS which may be forwarded to this office:—

3048, May 24th, 1918.
3051, July 5th, 1918.
3053, August 2nd, 1918.
3054, August 16th, 1918.
3056, September 13th, 1918.
3059, October 25th, 1918
3062, December 6th, 1918.
3063, December 20th, 1918.
3064, January 3rd, 1919.
3066, January 17th, 1919.
3068, January 31st, 1919.
3069, February 7th, 1919.
3070, February 14th, 1919.
3075, March 21st, 1919.

CHEMICAL NEWS OFFICE, 97, SHOE LANE, LONDON, E.C.4.

# THE CHEMICAL NEWS.

VOL. CXXII., No. 3170.

## EDITORIAL.

THE following papers have been received :—

"An Improvement in the Nomenclature of Organic Chemistry." By T. SHERLOCK WHEELER, A.R.C.Sc., A.I.C.

Some suggestions for a uniform system in which the names of compounds shall be connected with their formulæ, put forward in hope that the matter may claim the attention of those in the forefront of chemistry, and the possible formation of an International Congress to take up the subject upon lines similar to the Committee of Atomic Weights. Received January 6, 1921.

"The Storing of Light." By J. FREDERICK CORRIGAN.

The author's intention is to deal with the subject in two papers. The first gives an historical review of inorganic phosphorescence, from very early time to the dawn of modern science and the second will deal with the varied phenomena of phosphorescence and the modern theories which have been put forward to explain its cause. Received January 6, 1921.

## POLYMERISATION IN THE SOLID STATE.

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*Introductory Note.*

THIS paper is a continuation of "Aggregation at the Melting-Point" begun in CHEMICAL NEWS, vol. cxx., No. 3136. The formula I obtained

$$\frac{M.P. \times s}{R} = 4 \cdot 15$$

was based on the assumption that iodine and bromine were not associated at their melting-points and as a consequence I concluded that ice (at 0° C.) was $(H_2O)_2$. There is a consensus of opinion that ice is really $(H_2O)_3$ at its melting-point so that $p$ for iodine and bromine will be 1·5 and not 1. All values of $p$ (in the solid state) should, therefore, be calculated from

$$\frac{M.P. \times s}{R} = 6 \cdot 22$$

The results for ice (from 53°A to 273°A) are given in Table XXIV.

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As the specific heats of most elements have not been determined at their melting-points, $p$ has been calculated at the temperature of observation by substituting in

$$\frac{T \times St}{Rt} = 6 \cdot 22$$

where T is the temperature of observation on the absolute scale, and Rt is the rate of aggregation of a substance whose melting point is T. For, since

$$\frac{M.P. \times s}{R} = 6 \cdot 22$$

then

$$\frac{T \times s}{\frac{R \times T}{M.P.}} = 6 \cdot 22$$

∴ $R_T$, corresponding to T, is approximately equal to $\frac{R \times T}{M.P.}$

The results for diamond and graphite are given in Tables I. and II. respectively.

TABLE I.

| Absolute Temp. | RT. | ST. | Sols. | $p$. |
|---|---|---|---|---|
| 222 | 27·5 | 0·7711 | 0·0635 | 12·1 |
| 262·4 | 33 | 0·7840 | 0·0955 | 8·20 |
| 283·7 | 36 | 0·789 | 0·1128 | 7·00 |
| 306·4 | 39·3 | 0·7983 | 0·1318 | 6·06 |
| 331 | 43·3 | 0·814 | 0·1532 | 5·3 |
| 358·5 | 48 | 0·8322 | 0·1765 | 4·71 |
| 413 | 55 | 0·829 | 0·2218 | 3·73 |
| 479 | 63·8 | 0·829 | 0·2733 | 3·03 |
| 520 | 69 | 0·8259 | 0·3026 | 2·73 |
| 880 | 122 | 0·8629 | 0·4408 | 1·95 |
| 1080 | 150 | 0·864 | 0·4489 | 1·92 |
| 1258 | 174 | 0·861 | 0·4589 | 1·88 |

TABLE II.

| | | | | |
|---|---|---|---|---|
| 223 | 27·7 | 0·7732 | 0·1138 | 6·80 |
| 262 | 33 | 0·7840 | 0·1437 | 5·45 |
| 284 | 36 | 0·789 | 0·1604 | 4·92 |
| 334 | 43·8 | 0·8163 | 0·1990 | 4·1 |
| 411·5 | 54·8 | 0·828 | 0·2542 | 3·25 |
| 475 | 63 | 0·8256 | 0·2966 | 2·77 |
| 522 | 69 | 0·8259 | 0·3250 | 2·55 |
| 915 | 128 | 0·8707 | 0·4454 | 1·95 |
| 1095 | 151 | 0·8583 | 0·4539 | 1·89 |
| 1250 | 172 | 0·856 | 0·4670 | 1·83 |

The results for boron, beryllium, and silicon are given without comment in Table III.

TABLE III.

| Element | Absolute Temp. | ST. | Sols. | $p$. |
|---|---|---|---|---|
| Boron (amorph.) ... | 138 | 0·812 | 0·0707 | 11·5 |
| Boron (amorph.) ... | 235 | 0·825 | 0·1677 | 4·92 |
| Boron (cryst.) ... | 323 | 0·886 | 0·2518 | 3·51 |
| Beryllium ... ... | 296 | 1·057 | 0·397 | 2·66 |
| Beryllium ... ... | 323 | 1·08 | 0·4246 | 2·54 |
| Beryllium ... ... | 423 | 1·111 | 0·5060 | 2·19 |
| Beryllium ... ... | 530 | 1·095 | 0·582 | 1·88 |
| Silicon (amorph.) ... | 138 | 0·315 | 0·0913 | 3·45 |
| Silicon (cryst.) ... | 138 | 0·315 | 0·0861 | 3·66 |
| Silicon (cryst.) ... | 505 | 0·352 | 0·2029 | 1·72 |

In the following Tables (IV.—X.) the elements are treated from the point of view of the Periodic Classification.

TABLE IV.

| Element. | Absolute Temp. | ST. | Sols. | $p$. |
|---|---|---|---|---|
| Lithium ... ... | 137 | 1·272 | 0·521 | 2·43 |
| Lithium ... ... | 386 | 1·41 | 0·941 | 1·5 |
| Sodium ... ... | 262 | 0·4056 | 0·2934 | 1·38 |
| Potassium ... ... | 234 | 0·2367 | 0·1666 | 1·42 |
| Copper ... ... | 330 | 0·1551 | 0·0933 | 1·67 |
| Copper ... ... | 405 | 0·1584 | 0·0968 | 1·64 |
| Silver ... ... | 100 | 0·0759 | 0·0467 | 1·62 |
| Silver ... ... | 400 | 0·093 | 0·0572 | 1·62 |
| Silver ... ... | 700 | 0·0921 | 0·059 | 1·56 |

The values for silver are very consistent.

TABLE V.

| Element | Absolute Temp. | ST. | Sols. | $p$. |
|---|---|---|---|---|
| Beryllium... ... ... | See Table III. | | | |
| Magnesium ... | 308 | 0·405 | 0·245 | 1·65 |
| Calcium ... . . | 323 | 0·243 | 0·1804 | 1·35 |
| Zinc ... ... ... | 306 | 0·1476 | 0·0932 | 1·58 |
| Cadmium .. ... | 323 | 0·087 | 0·0548 | 1·59 |
| Mercury ... ... | 214 | 0·0465 | 0·0319 | 1·45 |

TABLE VI.

| | | | | |
|---|---|---|---|---|
| Boron... ... ... ... | See Table III. | | | |
| Aluminium ... | 100 | 0·305 | 0·1226 | 2·49 |
| Aluminium ... | 200 | 0·345 | 0·1731 | 2 |
| Aluminium ... | 300 | 0·3534 | 0·2053 | 1·72 |
| Aluminium ... | 700 | 0·369 | 0·2531 | 1·45 |
| Gallium ... ... | 291 | 0·135 | 0·079 | 1·71 |
| Iridium ... ... | 323 | 0·848 | 0·569 | 1·49 |

While $p$ for silver only falls from 1·62 to 1·56 between 100°A and 700°A, $p$ for aluminium falls from 2·49 to 1·45 for the same range of temperature. In the latter case the specific heat increases much more rapidly than in the former case.

TABLE VII.

| Element | Absolute Temp. | ST. | Sols. | $p$ |
|---|---|---|---|---|
| Carbon ... ... ... | See Tables I. and II. | | | |
| Silicon ... ... ... | See Table III. | | | |
| Tin ... ... ... | 323 | 0·0817 | 0·0545 | 1·5 |
| Lead ... ... ... | 240 | 0·0445 | 0·0306 | 1·45 |
| Lead ... ... ... | 307 | 0·463 | 0·0315 | 1·47 |

TABLE VIII.

| | | | | |
|---|---|---|---|---|
| Phosphorus (yellow) | 189 | 0·286 | 0·169 | 1·70 |
| Phosphorus (yellow) | 266 | 0·3 | 0·1788 | 1·68 |
| Phosphorus (yellow) | 298 | 0·309 | 0·202 | 1·53 |
| Phosphorus (red) | 298 | 0·309 | 0·1829 | 1·67 |
| Phosphorus (red) | 340 | 0·3167 | 0·2121 | 1·49 |
| Arsenic (cryst.) ... | 318 | 0·13 | 0·0830 | 1·56 |
| Arsenic (amorph.) | 316 | 0·13 | 0·0758 | 1·71 |
| Antimony ... ... | 186 | 0·076 | 0·045 | 1·68 |
| Antimony ... ... | 383 | 0·0846 | 0·0503 | 1·68 |
| Bismuth ... ... | 307 | 0·462 | 0·0305 | 1·51 |

Generally, $p$ for the amorphous element is higher than for the crystalline variety and where an element exists in two crystalline forms (cf. carbon) the values are by no means the same.

TABLE IX.

| Element. | Absolute Temp. | ST. | Sols. | $p$. |
|---|---|---|---|---|
| Sulphur (rhomb.) | 83 | 0·248 | 0·0835 | 2·95 |
| Sulphur (rhomb.) | 304 | 0·299 | 0·163 | 1·83 |
| Sulphur (monoclinic) | 289 | 0·295 | 0·1774 | 1·66 |
| Selenium (cryst.) ... | 315 | 0·1221 | 0·084 | 1·45 |
| Selenium (amorph.) | 301 | 0·1204 | 0·0953 | 1·26 |
| Selenium (amorph.) | 312 | 0·1218 | 0·1125 | 1·08 |
| Tellurium ... ... | 100 | 0·0648 | 0·0462 | 1·39 |
| Tellurium ... ... | 200 | 0·0735 | 0·0471 | 1·56 |
| Tellurium ... ... | 300 | 0·075 | 0·0480 | 1·56 |
| Tellurium ... ... | 400 | 0·0781 | 0·0489 | 1·59 |
| Tellurium ... ... | 500 | 0·0774 | 0·0498 | 1·56 |
| Tellurium ... ... | 600 | 0·078 | 0·0507 | 1·54 |
| Tellurium ... ... | 700 | 0·078 | 0·0516 | 1·51 |
| Chromium ... ... | 309 | 0·1853 | 0·0997 | 1·86 |

$p$, for sulphur is only 1·83 even at 304°A, so that it consists mainly of $S_2$ molecules. Tellurium behaves rather erratically, $p$ gradually increasing to 400°A, after which it gradually decreases to 700°A.

TABLE X.

| Element | Absolute Temp. | ST. | Sols. | $p$. |
|---|---|---|---|---|
| Iron ... ... ... | 273 | 0·1688 | 0·1116 | 1·5 |
| Iron ... ... ... | 323 | 0·1734 | 0·1124 | 1·54 |
| Iron ... ... ... | 373 | 0·1803 | 0·1138 | 1·58 |
| Iron ... ... ... | 473 | 0·1789 | 0·1189 | 1·5 |
| Iron ... ... ... | 573 | 0·1759 | 0·1267 | 1·39 |
| Iron ... ... ... | 773 | 0·1818 | 0·1366 | 1·33 |
| Iron (Temp. of Recalescence) ... | 920+ | | | |
| Iron ... ... ... | 1123 | 0·1839 | 0·1699 | 1·08 |
| Iron ... ... ... | 1273 | 0·1808 | 0·1678 | 1·08 |
| Cobalt ... ... | 326 | 0·165 | 0·1067 | 1·54 |
| Nickel ... ... | 100 | 0·1401 | 0·0575 | 2·43 |
| Nickel ... ... | 200 | 0·159 | 0·0878 | 1·82 |
| Nickel ... ... | 300 | 0·1624 | 0·1054 | 1·54 |
| Nickel ... ... | 400 | 0·1696 | 0·1168 | 1·45 |
| Nickel ... ... | 500 | 0·168 | 0·1233 | 1·37 |
| Nickel (critical Temp.) | 623 ? | | | |
| Nickel ... ... | 900 | 0·1773 | 0·1338 | 1·32 |
| Nickel ... .. | 1073 | 0·1768 | 0·1484 | 1·19 |
| Nickel ... ... | 1273 | 0·1749 | 0·1608 | 1·09 |
| Ruthenium .. | 323 | 0·0954 | 0·0611 | 1·56 |
| Palladium .. | 323 | 0·0912 | 0·0592 | 1·53 |
| Palladium ... | 905 | 0·0977 | 0·0714 | 1·37 |
| Osmium ... ... | 329 | 0·051 | 0·0311 | 1·63 |
| Iridium . ... | 323 | 0·0505 | 0·0323 | 1·56 |
| Iridium ... ... | 973 | 0·054 | 0·0401 | 1·35 |
| Platinum .. . . | 323 | 0·0496 | 0·0323 | 1·53 |
| Platinum ... ... | 773 | 0·0523 | 0·0377 | 1·38 |
| Platinum ... ... | 1673 | 0·054 | 0·0390 | 1·38 |
| Platinum ... ... | 1873 | 0·056 | 0·0398 | 1·39 |

The most interesting element in this group is iron. The value of $p$ gradually increases to 373°A, after which it diminishes. During recalescence new groupings of the atoms evidently take place for at 1173°A $p$ is only three quarters of its former value; *i.e.*, there is a sudden change in the value of $p$ from 1·33 to 1·08, when iron consists almost entirely of $Fe_1$ molecules. Now it is known that iron particles are more susceptible to new groupings than the molecules of any other element. An iron bar hammered in a magnetic field becomes magnetised through the arrangement of like poles in one direction; but heat or rough usage causes these temporary groupings to break up again and they disappear or become impossible above 983°A, at which temperature there is evidently no molecular complexity. It will be noticed that nickel does not behave in quite the same way unless its critical temperature is above 900°A (as in the case of iron).

To sum up: (1) Elements which have abnormal specific heats (elements of low atomic weights) are just those elements whose rate of change of $p$ per degree is considerable.

(2) For most elements $p$ diminishes as the temperature rises, and often, in the same group, as the atomic weight increases. An exception to the latter rule is exhibited by the triad iron, ruthenium, osmium, although this exception might disappear at the melting points (corresponding temperatures).

(3) Iron appears to behave normally until its critical temperature, when it suddenly changes from a mixture of $Fe_2$ and $Fe_1$ molecules to $Fe_1$ molecules.

(4) The values of R at the melting-points are relative to $Br_5$. The values of $R_T$ quoted in this paper are equal to

$$\frac{R \times T}{M.P.}$$

The lower the temperature the smaller does R appear to be, and the greater is the value of $p$ for any substance. At the absolute zero a substance will be incapable of aggregating but with increase of temperature the power to do so returns. On the other hand $p$ will have its maximum value at the absolute zero. We might illustrate this phenomenon by the analogy of a siege. The people of the land represent an aggregation of units, more or less organised for defence. As the size of the aggregation (RT) diminishes through casualties (starvation) the better organised ($p$) must the remnant become to resist the onslaughts of the enemy. Individual tastes and pursuits are sacrificed and even the individual identity is lost in the interests of the State. So, on approaching the absolute zero, when the power of aggregation has almost passed away, the atoms or molecules show their greatest degree of coalescence.

*Polymerisation amongst Compounds.*

Most, if not all, elements polymerise, but this property is shown more particularly by the elements in the first two rows, and they are able to exert their polymerising influence in their compounds. The results for the chlorides are given in Table XI.

TABLE XI.

| Compound | Absolute Temp. | ST. | Sols. | $p$. |
|---|---|---|---|---|
| LiCl ... ... ... | 328 | 0·456 | 0·282 | 1·62 |
| NaCl ... ... ... | 330 | 0·333 | 0·214 | 1·56 |
| KCl ... ... ... | 330 | 0·264 | 0·173 | 1·53 |
| RbCl ... ... ... | 303 | 0·157 | 0·112 | 1·40 |
| $Cu_2Cl_2$ ... ... | 331 | 0·199 | 0·138 | 1·44 |
| AgCl ... ... ... | 330 | 0·1354 | 0·0911 | 1·48 |
| $NH_4Cl$ ... ... | 303 | 1·072 | 0·373 | 2·88 |
| $MgCl_2$ ... ... | 304 | 0·303 | 0·191 | 1·59 |
| $CaCl_2$ ... ... ... | 334 | 0·264 | 0·164 | 1·60 |
| $CaCl_2.6H_2O$ ... | 264 | 0·927 | 0·345 | 2·68 |
| $CaCl_2.6H_2O$ ... | 289 | 0·905 | 0·647 | 1·39 |
| $SrCl_2$ ... ... ... | 329 | 0·184 | 0·120 | 1·53 |
| $BaCl_2$ ... ... | 329 | 0·143 | 0·0896 | 1·59 |
| $BaCl_2.2H_2O$ ... | 305 | 0·353 | 0·171 | 2·05 |
| $ZnCl_2$ ... ... | 333 | 0·217 | 0·136 | 1·59 |
| $Hg_2Cl_2$ ... ... | 326 | 0·082 | 0·052 | 1·58 |
| $HgCl_2$ ... ... | 329 | 0·108 | 0·0689 | 1·56 |
| $TiCl_4$ ... ... ... | 329 | 0·255 | 0·188 | 1·35 |
| $SnCl_2$ ... ... ... | 333 | 0·155 | 0·1016 | 1·51 |
| $SnCl_4$ ... ... | 329 | 0·190 | 0·1476 | 1·29 |
| $PbCl_2$ ... ... | 333 | 0·106 | 0·0665 | 1·59 |
| $PCl_3$ ... ... ... | 328 | 0·285 | 0·209 | 1·36 |
| $AsCl_3$ ... ... | 329 | 0·216 | 0·176 | 1·23 |
| $CuK_2Cl_42H_2O$ ... | 308 | 0·393 | 0·197 | 2·00 |
| $K_2PtCl_6$ ... ... | 303 | 0·175 | 0·113 | 1·55 |
| $K_2ZnCl_4$ ... ... | 305 | 0·234 | 0·152 | 1·55 |
| $K_2SnCl_6$ ... ... | 308 | 0·21 | 0·133 | 1·58 |

The chlorides appear to polymerise to about the same extent as the elements composing them, but the presence of water leads to further polymerisation, the value of $CaCl_2.6H_2O$ being 2·68 at 264° A. This value drops to 1·39 at 289° A, due perhaps, to dissociating into anhydrous $CaCl_2$ and free (liquid) water whose $p$'s are 1.60 and 1+ respectively. Three double chlorides have the $p$'s of the separate chlorides. The most interestin compound in the list is ammonium chloride whic appears to be $N_3H_{12}Cl_3$ or a mixture of $N_2H_8C$ and $N_4H_{16}Cl_4$.

The bromides and iodides give similar result but the fluorides are slightly more polymerisec for fluorine can claim to be a polymerising agen (compare $\mathbf{H_nF_n}$ where the complex molecules ar probably due to both H and F). See Table XII

TABLE XII.

| Compound | Absolute Temp. | ST. | Sols. | p. |
|---|---|---|---|---|
| $CaCl_2$ ... ... | 334 | | | 1·6 |
| $K_2ZnCl_4$ ... ... | 305 | | | 1·5 |
| $CaF_2$ ... ... ... | 309 | 0·370 | 0·209 | 1·7 |
| $AlNa_3F_6$ ... ... | 309 | 0·459 | 0·238 | 1·9 |

It has previously been shown that sulphur doe not polymerise to anything like the same exten as carbon, boron, &c. do ($p = 1·83$ at 304° A) an this fact is comfirmed by determining $p$ for th sulphides (Table XIII).

TABLE XIII.

| Compound | Absolute Temp. | ST. | Sols. | $p$. |
|---|---|---|---|---|
| $Cu_2S$ ... ... ... | 309 | 0·183 | 0·120 | 1·53 |
| $Ag_2S$ ... ... ... | 326 | 0·1177 | 0·0746 | 1·57 |
| ZnS ... ... ... | 304 | 0·1975 | 0·120 | 1·6 |
| HgS ... ... ... | 309 | 0·0829 | 0·0517 | 1·59 |
| SnS ... ... ... | 329 | 0·1293 | 0·0836 | 1·5 |
| $SnS_2$ ... ... ... | 327 | 0·159 | 0·1193 | 1·3 |
| PbS ... ... ... | 305 | 0·080 | 0·049 | 1·6 |
| $Sb_2S_3$ ... ... ... | 334 | 0·145 | 0·084 | 1·7 |
| $Bi_2S_3$ ... ... ... | 328 | 0·094 | 0·060 | 1·5 |
| FeS ... ... ... | 331 | 0·222 | 0·1357 | 1·6 |
| $FeS_2$ ... ... ... | 305 | 0·24 | 0·1255 | 1·9 |
| NiS ... ... ... | 329 | 0·214 | 0·128 | 1·6 |
| $CuFeS_2$ ... ... | 307 | 0·210 | 0·131 | 1·0 |

Whereas the raising of FeS to $FeS_2$ increase $p$ from 1·62 to 1·90, increasing the valency has the opposite effect in the case of the sulphides of tir (cf. $SnCl_2$ and $SnCl_4$). This might point to the presence of $SnS_2$, SnS, and S even at ordinary temperatures, for when $SnS_2$ is heated, " a portion sublimes without decomposition but the greater part is resolved into sulphur and the monosulphide" (Roscoe and Schorlemmer, "Treatise on Chemistry," vol. ii., p. 846).

Table XIV. gives the results for the sulphate and it will be seen how the presence of oxygen and hydrogen (both polymerising agents) leads to greater polymerisation.

TABLE XIV.

| Compound | Absolute Temp. | ST. | Sols. | $p$. |
|---|---|---|---|---|
| $(NH_4)_2SO_4$ ... | 302 | 1·086 | 0·350 | 3·10 |
| $Na_2SO_4$ ... ... | 315 | 0·477 | 0·229 | 2·09 |
| $K_2SO_4$ ... ... | 329 | 0·393 | 0·190 | 2·07 |
| $KHSO_4$ ... ... | 308 | 0·490 | 0·244 | 2·02 |
| $CuSO_4$ ... ... | 335 | 0·369 | 0·184 | 2·00 |
| $CuSo_4.5H_2O$ ... | 305 | 0·81 | 0·285 | 2·83 |
| $CuSo_4.5H_2O$ ... | 335 | 0·826 | 0·316 | 2·61 |
| $MgSO_4$ ... ... | 335 | 0·490 | 0·225 | 2·17 |
| $MgSO_4.7H_2O$ ... | 304 | 1·051 | 0·362 | 2·91 |
| $CaSO_4$ ... ... | 305 | 0·423 | 0·178 | 2·37 |
| $CaSO_42H_2O$ ... | 304 | 0·667 | 0·259 | 2·58 |
| $BaSO_4$ ... ... | 306 | 0·247 | 0·108 | 2·28 |
| $BaSO_4$ ... ... | 327 | 0·251 | 0·1128 | 2·22 |
| $PbSO_4$ ... ... | 308 | 0·190 | 0·0827 | 2·29 |
| $FeSO_4.7H_2O$ ... | 305 | 0·931 | 0·346 | 2·70 |
| $CoSO_4.7H_2O$ ... | 295 | 0·914 | 0·343 | 2·67 |

The conversion of a sulphide into a sulphate raises $p$ from about 1·65 to 2+ (for anhydrous salts), a tribute to the polymerising properties of oxygen. The presence of water of crystallisation still further increases $p$. Ammonium sulphate is

$$\left\{ (NH_4)_2SO_4 \right\}_3$$

or a mixture of $(NH_4)_4S_2O_8$ and $(NH_4)_8S_4O_{16}$.

The results for a few hyposulphites are given in Table XV.

TABLE XV.

| Compound | Absolute Temp. | ST. | Sols. | $p$. |
|---|---|---|---|---|
| $Na_2S_2O_3$ ... ... | 335 | 0·435 | 0·221 | 1·96 |
| $Na_2S_2O_3.5H_2O$ ... | 301 | 0·847 | 0·445 | 1·90 |
| $K_2S_2O_3$ ... ... | 333 | 0·360 | 0·197 | 1·83 |
| $BaS_2O_3$ ... ... | 331 | 0·235 | 0·163 | 1·44 |
| $PbS_2O_3$ ... ... | 331 | 0·185 | 0·092 | 2·00 |

The hydrated sodium salt is less polymerised than the anhydrous salt, surely a rare occurrence, although it should be pointed out that the specific heats have been supplied by different observers. The low value for the hydrated salt may be due to partial decomposition, decomposition into $Na_2S_2O_3$ and $H_2O$ (whose $p$'s are 1·96 and 1+ respectively).

The hyposulphates are less polymerised than the corresponding sulphates owing to the substitution of a sulphur atom for a more highly polymerising oxygen atom.

We should expect the borates, which contain two highly polymerising elements, boron and oxygen, to be more highly polymerised than the sulphates, and this surmise is confirmed by the results quoted in Table XVI.

TABLE XVI.

| Compound | Absolute Temp. | ST. | Sols. | $p$. |
|---|---|---|---|---|
| $KBO_2$ ... ... | 329 | 0·477 | 0·2048 | 2·32 |
| $NaBO_2$ ... ... | 330 | 0·592 | 0·2571 | 2·31 |
| $Pb(BO_2)_2$ ... ... | 329 | 0·232 | 0·090 | 2·58 |
| $Na_2B_4O_7$ ... ... | 305 | 0·616 | 0·229 | 2·70 |
| $Na_2B_4O_7$ ... ... | 329 | 0·627 | 0·238 | 2·62 |
| $Na_2B_4O_7.10H_2O$ | 308 | 1·083 | 0·385 | 2·82 |
| $K_2B_4O_7$ ... ... | 331 | 0·543 | 0·2198 | 2·48 |
| $PbB_4O_7$ ... ... | 329 | 0·322 | 0·114 | 2·82 |

The bigger the percentage of polymerising atoms present, the more polymerised is the salt. This fact is very obvious from the lead salts (sulphur is not included as a polymerising agent as its $p$ is only a little more than that of lead).

| Compound | Percentage of Polymerising Atoms (Boron and Oxygen) | $p$. |
|---|---|---|
| $PbCl_2$ ... ... | 0 | 1·59 |
| $PbS$ ... ... | 0 | 1·62 |
| $PbS_2O_3$ ... ... | 50 | 2·00 |
| $PbSO_4$ ... ... | 67 | 2·25 |
| $PbB_2O_4$ ... | 86 | 2·58 |
| $PbB_4O_7$ ... | 92 | 2·82 |

We have seen the effect of a basic polymerising radicle $(NH_4)$ in ammonium chloride (where $p$=2·88) and ammonium sulphate, which contains both a basic and an acidic $(SO_4)$ polymerising radicle ($p$=3·10). What will be the effect of the juxtaposition of the ammonium and the nitric acid radicles? See Table XVII.

TABLE XVII.

| Compound | Absolute Temp. | ST. | Sols. | $p$. |
|---|---|---|---|---|
| $NH_4O_3$ ... ... | 295 | 1·071 | 0·455 | 2·35 |
| $NaNO_3$ ... ... | 316 | 0·57 | 0·265 | 2·15 |
| $NaNO_3$ ... ... | 329 | 0·575 | 0·278 | 2·07 |
| $KNO_3$ ... ... | 303 | 0·474 | 0·232 | 2·04 |
| $KNO_3$ ... ... | 329 | 0·483 | 0·239 | 2·03 |
| $AgNO_3$ ... ... | 330 | 0·286 | 0·1435 | 2·00 |
| $Sr(NO_3)_2$ ... ... | 305 | 0·408 | 0·181 | 2·25 |
| $Ba(NO_3)_2$ ... ... | 305 | 0·330 | 0·145 | 2·28 |
| $Ba(NO_3)_2$ ... ... | 329 | 0·336 | 0·1523 | 2·19 |
| $Pb(NO_3)_2$ ... ... | 305 | 0·259 | 0·110 | 2·35 |
| $Pb(NO_3)_2$ ... ... | 331 | 0·266 | 0·1173 | 2·26 |

$p$ for nitrates lies between the values for the chlorides and the sulphates, except in the case of ammonium nitrate.

Results for a few phosphates, chromates, chlorates, and arsenates are given in Tables XVIII., XIX., XX., XXI. respectively.

TABLE XVIII.

| Compound | Absolute Temp. | ST. | Sols. | $p$. |
|---|---|---|---|---|
| $KH_2PO_4$ ... ... | 305 | 0·564 | 0·208 | 2·71 |
| $Na_2HPO_3.12H_2O$ | 264 | 1·145 | 0·454 | 2·52 |
| $NaPO_3$ ... ... | 303 | 0·469 | 0·217 | 2·16 |
| $Ca(PO_3)_2$ ... ... | 329 | 0·444 | 0·199 | 2·24 |
| $Na_4P_2O_7$ ... ... | 330 | 0·479 | 0·228 | 2·09 |
| $K_4P_2O_7$ ... ... | 330 | 0·385 | 0·191 | 2·01 |
| $Pb_2P_2O_7$ ... ... | 327 | 1·822 | 0·821 | 2·22 |

TABLE XIX.

| | | | | |
|---|---|---|---|---|
| $K_2CrO_4$ ... ... | 306 | 0·345 | 0·189 | 1·83 |
| $K_2Cr_2O_7$ ... ... | 309 | 0·359 | 0·186 | 1·92 |
| $PbCrO_4$ ... ... | 308 | 0·179 | 0·090 | 1·98 |

TABLE XX.

| | | | | |
|---|---|---|---|---|
| KCl ... ... ... | — | — | — | 1·53 |
| $KClO_3$ ... ... | 307 | 0·391 | 0·194 | 2·01 |
| $KClO_4$ ... ... | 303 | 0·415 | 0·190 | 2·19 |
| $Ba(ClO_3)_2.H_2O$ | 305 | 0·357 | 0·157 | 2·26 |

TABLE XXI.

| | | | | |
|---|---|---|---|---|
| $KAsO_3$ ... ... | 331 | 0·301 | 0·156 | 1·92 |
| $KH_2AsO_4$ ... ... | 304 | 0·426 | 0·175 | 2·43 |
| $Pb_3(AsO_4)_2$ ... | 328 | 0·141 | 0·0728 | 1·94 |

Table XXII., which concerns the carbonates, is interesting as it shows the various forms of calcium carbonate to be almost equally polymerised.

TABLE XXII.

| Compound | Absolute Temp. | ST. | Sols. | $p$. |
|---|---|---|---|---|
| $Na_2CO_3$ ... ... | 306 | 0·543 | 0·246 | 2·20 |
| $Na_2CO_3$ ... ... | 330 | 0·552 | 0·2727 | 2·02 |
| $K_2CO_3$ ... ... | 305 | 0·417 | 0·206 | 2·02 |
| $K_2CO_3$ ... ... | 334 | 0·426 | 0·216 | 1·97 |
| $Rb_2CO_3$ ... ... | 305 | 0·249 | 0·123 | 2·02 |
| $CaCO_3$: | | | | |
| Calespar ... | 305 | 0·479 | 0·206 | 2·33 |
| Arragonite ... | 303 | 0·479 | 0·203 | 2·35 |
| Marble (white | 330 | 0·489 | 0·216 | 2·26 |
| Marble (grey) ... | 333 | 0·489 | 0·210 | 2·33 |
| $SrCO_3$ ... ... | 326 | 0·33 | 0·1475 | 2·24 |
| $BaCO_3$ ... ... | 328 | 0·248 | 0·1104 | 2·24 |
| $PbCO_3$ ... ... | 305 | 0·179 | 0·0791 | 2·25 |
| $FeCO_3$ ... ... | 326 | 0·42 | 0·1934 | 2·16 |

Table XXIII. is an attempt to arrange the salts of potassium and lead in the order of $p$. Perhaps, this order will not hold good for the acids themselves, which will have still higher values. *E.g.*,

from the specific heats of sulphuric acid at 243° A and 273°A, $p$ is 2·80 and 2·48 respectively.

TABLE XXIII.

| Acid | $p$. Pb. | $p$. $k$ |
|---|---|---|
| $H_2B_4O_7$ ... | 2·82 | 2·48 |
| $HBO_2$ .. | 2·58 | 2·32 |
| $HCLO_4$ .. | — | 2·19 |
| $HgSO_4$ .. | 2·29 | 2·07 |
| $HNO_3$ ... | 2·35 | 2·04 |
| $H_2CO_3$ ... | 2·25 | 2·02 |
| $HClO_3$ ... | — | 2·01 |
| $H_4P_2O_7$ .. | 2·22 | 2·01 |
| $H_2CrO_4$ ... | 1·98 | 1·83 |
| $H_2S_2O_3$ ... | 2·00 | 1·83 |
| $H_2S$ ... .. | 1·62 | — |
| HCl ... .. | 1·59 | 1·53 |

The values of $p$ for a number of oxides are given in Table XXIV. $p$ is highest for $B_2O_3$, $Co_2$, and $H_2O$ which are composed of highly polymerising elements. The addition of an atom of oxygen (MnO to $MnO_2$) has the effect of raising $p$ from 1·74 to 2·07.

TABLE XXIV.

| Compound | Absolute Temp. | ST. | Sols. | $p$. |
|---|---|---|---|---|
| $Cu_2O$ ... .. ... | 308 | 0·201 | 0·111 | 1·81 |
| CuO ... ... ... | 308 | 0·243 | 0·128 | 1·89 |
| MgO ... ... ... | 335 | 0·490 | 0·2439 | 2·01 |
| $Mg(OH)_2$ ... ... | 308 | 0·828 | 0·312 | 2·65 |
| ZnO ... ... ... | 330 | 0·241 | 0·1248 | 1·94 |
| HgO ... ... ... | 308 | 0·0888 | 0·053 | 1·68 |
| $B_2O_3$ ... ... .. | 330 | 0·698 | 0·2374 | 2·94 |
| $Al_2O_3$ (corundum) | 327 | 0·475 | 0·1976 | 2·40 |
| $Al_2O_3$ (sapphire) | 326 | 0·475 | 0·2173 | 2·18 |
| $SiO_2$ (quartz) ... | 308 | 0·481 | 0·186 | 2·59 |
| $SiO_2$ (opal) ... ... | 309 | 0·481 | 0·185 | 2·59 |
| $SiO_2$ (Hyalith) ... | 306 | 0·48 | 0·1755 | 2·73 |
| $TiO_2$ ... ... ... | 330 | 0·366 | 0·1716 | 2·13 |
| $SnO_2$ ... ... ... | 305 | 0·190 | 0·0894 | 2·13 |
| $SnO_2$ (tinstone) .. | 330 | 0·194 | 0·0936 | 2·07 |
| PbO ... ... ... | 307 | 0·086 | 0·0553 | 1·56 |
| $As_2O_3$ ... ... ... | 328 | 0·2468 | 0·1276 | 1·94 |
| $Sb_2O_3$ ... ... ... | 332 | 0·1698 | 0·0927 | 1·83 |
| $Bi_2O_3$ ... ... ... | 328 | 0·105 | 0·0609 | 1·72 |
| $Cr_2O_3$ ... ... .. | 309 | 0·31 | 0·177 | 1·79 |
| $MoO_3$ ... ... ... | 305 | 0·2662 | 0·154 | 1·72 |
| $WO_3$ ... ... ... | 310 | 0·166 | 0·0894 | 1·85 |
| MnO ... ... ... | 329 | 0·275 | 0·157 | 1·74 |
| $MnO_2$ ... ... ... | 305 | 0·330 | 0·159 | 2·07 |
| $Fe_3O_4$ ... ... | 305 | 0·289 | 0·156 | 1·85 |
| $Fe_2O_3$ ... ... ... | 305 | 0·3 | 0·1565 | 1·90 |
| $MgAl_2O_4$ (spinelle) | 304 | 0·472 | 0·194 | 2·43 |
| $CaSiO_3$ (wollastonite) | 308 | 0·414 | 0·178 | 2·32 |
| $ZrSiO_4$ (zircon) ... | 309 | 0·315 | 0·132 | 2·39 |
| $CO_2$ ... ... ... | 140 | 0·606 | 0·215 | 2·82 |
| $SO_2$ ... ... ... | 127 | 0·413 | 0·228 | 1·81 |
| $H_2O$ ... ... ... | 53 | 1·232 | 0·146 | 8·44 |
| $H_2O$ ... ... ... | 140 | 1·510 | 0·285 | 5·30 |
| $H_2O$ ... ... ... | 225 | 1·529 | 0·463 | 3·30 |
| $H_2O$ ... ... ... | 273 | 1·556 | 0·504 | 3·08 |

Ice will be about $(H_2O)_{12}$ at the absolute zero.

I intended in this article to make some reference to the main group of organic compounds, but the subject, though of great interest, must be reserved for some future occasion. A few results are given in Table XXV.

TABLE XXV.

| Compound | Absolute Temp. | ST. | Sols. | $p$ |
|---|---|---|---|---|
| $C_2Cl_6$ .. .. ... | 300 | 0·322 | 0·178 | 1·81 |
| $C_2Cl_6$ ... ... ... | 303 | 0·322 | 0·194 | 1·67 |
| $C_2Cl_6$ ... ... ... | 307 | 0·324 | 0·277 | 1·17 |
| $C_{12}H_{22}O_{11}$ . | | | | |
| (Crystalline) ... | 309 | 1·2775 | 0·3005 | 4·25 |
| (Amorphous) ... | 309 | 1·2775 | 0·342 | 3·74 |
| $C_6H_6$ ... ... ... | 223 | 1·416 | 0·262 | 5·40 |
| | 243 | 1·425 | 0·292 | 4·88 |
| | 263 | 1·437 | 0·376 | 3·82 |
| | 273 | 1·444 | 0·460 | 3·14 |
| | 273 | 1·444 | 0·397 | 3·64 |
| $C_{10}H_8$ .. ... ... | 223 | 1·294 | 0·240 | 5·39 |
| | 288 | 1·336 | 0·314 | 4·25 |
| | 318 | 1·369 | 0·326 | 4·20 |
| | 338 | 1·382 | 0·334 | 4·13 |

*To Calculate the Molecular Weight of a Solid Substance from its Specific Heat.*

By means of the specific heat the molecular weight of any solid substance (element or compound) can be determined with ease at any temperature without vapourising it. All that is necessary is a reliable knowledge of the behaviour of some pure solid which can serve as a standard. E.g., ice at 273°A. Now,

$$\frac{T \times s \text{ (calc.)}}{R} = 6{\cdot}22$$

$$\therefore\ T \times p \times s \text{ (ols.)} = 6{\cdot}22\ R$$

$$= 6{\cdot}22 \left\{ \frac{\text{Melticular Weight}}{\text{Formula Wt. of } H_2O} \times 3 \right\}$$

$$= \frac{6{\cdot}22 \times \text{Melticular Weight}}{\text{Average atomic weight of atoms present } (=6)}$$

$$\therefore\ 6T \times 3 \times {\cdot}5 = 6{\cdot}22 \times \text{Melticular Weight.}$$

$$\therefore\ 9T \quad = 6{\cdot}22 \times \text{Melticular Weight} \quad (1)$$

For any other substance ($x$) whose specific heat ($s_x$) is known at T the formula becomes

$$W_x \times T \times p_x \times S_x = 6{\cdot}22 \times \text{Melticular Weight,}$$

(2) where $W_x$ is the average atomic weight of atoms composing $x$.

Dividing (2) by (1)

$$p_x = \frac{9}{W_x \times S_x}$$

Thus, for any temperature,

$$p\ w\ s = \text{a constant,}$$

or, the "molecular" heat (*i.e.*, the polmericular heat) of any element or compound at any temperature is directly proportional to the number of atoms present and is independent of their nature.

*Example.*

What is the molecular weight of solid formic acid whose specific heat at 273°A is 0·430?

Here, $W_x = \frac{46}{5}$

$S_x = 0{\cdot}430$

$$\therefore\ p_x = \frac{9}{\frac{46}{5} \times 0{\cdot}430} = 2{\cdot}27$$

∴ Formic acid at 273°A is $(H.COOH)_2$.

This method of finding molecular weights can be applied to the liquid and gaseous states.

(To be continued.)

## HOW COAL WASTAGE INCREASES TUBERCULOSIS.*

By W. H. CASMEY.

WE are using nearly 200 million tons of coal per year, 25 per cent of which is wasted by stoking at the wrong time and giving approximately 80 per cent more air than is required for economically burning the coal, and it is the effect of this excess air used which has such a disastrous effect both on human life and vegetation.

Consider the earth as forming the base of a sea of air, the composition of which as before stated is 78 per cent nitrogen and 21 per cent oxygen and 1 per cent of other gases including 1 part of carbon dioxide in 2500 of air, and that to maintain health this proportion must be maintained within a margin of 3 parts $CO_2$ to 10,000 or air, in excess of normal conditions, say the maximum $CO_2$ in 10,000 must not exceed 7 parts.

The area of the British Isles is 121,000 square miles, and to keep our figures small it is proposed to take one square mile as a unit and we find we consume 1612 tons of coal per year for each square mile and when using coal on scientific lines 29,000 tons of air is required per square mile, say 845 million cubic feet. The coal consumption in Wakefield is 22,000 tons per square mile, and in Bradford 37,000 tons.

The atmosphere will absorb the carbon dioxide ($CO_2$) in the gases and gradually diffuse it and so maintain the standard 4 parts in 10,000 from which, as already inferred, vegetation is fed, but under general working conditions of 30 pounds of air per pound of coal the gases discharged into the atmosphere is 48,000 tons per square mile as against 29,000 tons, the result being that this overcharge which is accompanied by a large quantity of dust and products of imperfect combustion which fouls the atmosphere and does more in destroying both life and vegetation than any other cause, and in our industrial centres the dust fall during the year ranges from 400 to 600 tons per square mile, whereas in the suburbs the deposit is less than 30 tons.

Is there any wonder that under such conditions it is next to impossible to grow either flowers or fruit in such areas. Two hours' sunshine is taken from us per day with such a mass of floating dust and the lungs of plant life are choked. Why? Because we have not followed the Designer's law already given, and for these losses and annoyances we have only our stupid selves to blame.

If we could follow in burning coal the same laws of proportion as used in all our works and factories we could make no mistake, but the boiler house, the greenhouse and the house fires seldom receive any sensible consideration.

Under normal conditions the whole of the blood in the human body is brought into contact with the air once per minute, and the air we expire may very well be considered as the smoke from the boiler furnace, as the law of combustion as already stated, applies to both.

The parallel goes still further, the safety valve of the body is set at 98°, and no matter when in health if surrounded by air at 20° or 200°, the temperature of the blood never varies, in one case deeper breathing is carried on, which supplies more air to the body and therefore more heat is generated, and in the other case the heat escapes through the sweat glands in the form of moisture.

We take in when we breathe oxygen and expire $CO_2$, but if the outside air already holds more $CO_2$ than the standard 1 part in 2500, we are not maintaining the health of the body, as no matter how foul the air may be by which we are surrounded, we are compelled to breathe it. Here the senses of smell and taste cannot help us, whereas they enable us to reject impure food and drink.

By great care in our drainage schemes and water supplies, typhoid and typhus fevers are now practically unknown, and as the greater number of diseases are air-borne, every care should be taken to maintain a pure atmosphere, but what are we doing in this direction. The appointment of a smoke inspector appears to the authorities as the only thing necessary, but food and water inspection are considered of vital importance, and so they are, but not more so than the air we are compelled to breathe.

Let us now consider how an impure atmosphere affects us; take as an example one of our large schools accommodating say 1000 scholars.

In the act of breathing, $CO_2$ is expelled from the lungs and to dilute the expired air so that it contains not more than 7 parts of $CO_2$ in 10,000 of air, it is necessary to supply 3300 cubic feet of air per child per hour, or a total for the school of 3,300,000 cubic feet, so that impurities in the outside air are very much in evidence inside the school.

The air supply to this school equals 100 tons of air per hour, and without mechanical means it is not possible to secure it, and the result is, that as a rule, windows are opened and the outer air obeying the laws of gravitation merely falls through the windows, causing what we call draughts, resulting in colds to the youngsters near the windows, and even when the windows are closed, the so-called draughts continue, caused by the quick transmission of heat through the glass which is six times as rapid as through the walls, and every 10° fall in temperature increases the weight of a cubic foot of air 1 grain, the draught therefore is again a case of gravitation due to heat transmission.

We cannot burn coal to the best advantage without a proper air supply, nor maintain health either, and we have but few schools or public buildings in Yorkshire where anything like scientific ventilation is in use, coal is wasted due to havng too great a supply of air, life is wasted by not having a sufficient supply. There is no wonder that schools are often closed for weeks together due to the outbreak of infectious diseases directly caused through lack of fresh air. There, no doubt, tuberculosis often originates.

Every buildng should be so fitted up with heating and ventilating plant that the correct temperature and purity of air is maintained under all conditions and the ventilation such that the building breathes in unison with the number of people occupying it, and it is only by adopting the lines thus indicated that tuberculosis can be stamped out.

The late King Eward the VII., when addressing a conference on the subject of the fresh air cure for tuberculosis asked the pregnant question: "If preventable, why not prevented?" And we still await the answer.

*Extract from a Lecture given before the Wakefield Paxton Society, January 1st, 1921.

To save coal we must burn it, the outside air will then be kept pure; to prevent consumption every building where people are gathered together must be made equal to a fresh air hospital by heating and ventilation. Our trams and railway carriages must carry the number of people they are constructed to carry, and no more, and when we give the same attention to the air we are compelled to breathe as to our water and food supplies we shall have attained what has been attempted in a half-hearted way for many years; a kingdom free from coal wastage and tuberculosis.

In conclusion, let us draw the tangled cords together and we find a very simple problem. The law of combustion applies both to the human frame and the boiler furnace in one, oxygen is breathed in and $CO_2$ breathed out. Plant life takes in $CO_2$, but breathes out oxygen; $CO_2$ may therefore be considered as the link between the animate and inanimate kingdoms.

By careless burning of our coal we discharge other gases than $CO_2$ into the atmosphere and practically suffocate the weaker members of plant life, thus interfering both directly and indirectly with the Creator's design.

For months every newspaper has been giving columns on national economy, whatever that means, but little has been said of the foundation on which true economy is built.

Dear coal means dear metal, the machines made from these are proportionately dear, and so is the products they assist in producing. The reason is, because the demand for coal has exceeded the supplies, and our coal exports have fallen. If we all unite in using coal as it should be used, we should save 50 million tons per year; this would bring the supplies in excess of demands, with the natural results, easier prices; this would also enable us to again export more coals, thus bringing into our country cheaper produce, therefore, cheaper living, and the stability of the country would be in the direction of pre-war conditions.

The economy we require is not one made and practised in the House of Commons only, but made and practised daily in each one of our 8,000,000 houses and 40,000 works, and the result of such economy would be "reduction in coal consumption," "reduction of our death rate," and further, a big reduction in the cost of living. Remeber the three "R's" during 1921.

## PRESENT POSITION OF THE FINE CHEMICAL INDUSTRY.

By C. A. HILL.

THE British fine chemical industry is to-day in a critical position—a conditon resulting from a combination of circumstances. According as the Government redeems its pledge or not, the industry can either stabilise itself and become second to no other fine chemical industry in the world, or, alternatively, will sink back into its pre-war condition, or something very nearly like it.

The chemical industry consists of two parts:—(1) heavy chemicals; (2) fine chemicals. The former has several main branches, such as the acid, the alkali, and the soap industries; all of these were well-developed and well-organised British industries before the war. The latter has very many branches, but none was well-developed before the war, nor was the industry organised. Dyes constitute a group of fine chemicals, so large and important that they are generally considered as a separate branch of chemical industry; actually, however, they cannot be thus divorced from the rest of the fine chemical industry. Parliament is legislating for the dye industry; it must also legislate for the remainder, and no short-sighted policy should be allowed to interfere in this important national question.

Comparatively few people outside the profession of chemistry know what the fine chemical industry is; still less do they know of its many and far reaching ramifications, by reason of which it is essentially and truly a "key" industry, and therefore of vital importance to the national welfare. Before the war even chemists, generally, had rather vague notions as to what precisely fine chemicals are. How often has one heard such loose expressions as "medicinal and fine chemicals" or "fine chemicals and analytical reagents," and the like Indeed, a notorious Board of Trade memorandum, born a little more than a year ago and now decently interred, made use of the expression "analytical reagents and the following fine chemicals." "Fine chemicals" is the term comprehensive of *all* fine chemicals, and includes the various groups:—(1) laboratory chemicals (*i.e.*, analytical reagents and research chemicals); (2) medicinal (or pharmaceutical) chemicals; (3) photographic chemicals; together with other groups according to taste.

It is now well known that whereas before the war the manufacture of certain fine chemicals was satisfactorily established in this country, in the large sense, the fine chemical industry was essentially German. There was no organised industry and no organisation of manufacturers. To-day the Fine Chemical Group of the Association of British Chemical Manufacturers is numerically the strongest and possibly the most active in the Association.

The outbreak of war rudely awakened the country to the fact that fine chemicals are products of national importance, and, incidentally, that war cannot be waged without them, so that many and many a substance which we had until then contentedly bought from Germany had to be manufactured hurriedly with inappropriate plant and almost regardless of cost. Some of these were wanted for the immediate purposes of war, others for the manufacture of munitions, yet others for their medicinal properties. Arrangements prompted by the action of the Institute of Chemistry and the Society of Public Analysts were made for the supply of analytical reagents of requisite and known purity. More recently the manufacture of research chemicals has been systematically undertaken, and is now approaching a satisfactory condition. Good headway has been made by the makers of photographic chemicals, and also by those of synthetic perfumes and essences. The manufacture of medicinal organic synthetic products has made very considerable progress; those begun early have been improved, perfected, and stabilised; and many others have been added or were in course of being added when the present *impasse* arose. It is much to be able to say that we have never gone short of essentials. British manufacturers have proved that they can

turn out products of first-rate quality. Economy of manufacture, maximum yields, with corresponding reduction of costs, were following in due course, slowly, it is true, but nevertheless surely.

Rome was not built in a day. To train up an army of skilled organic chemical workers requisite to the fine chemical industry is a matter of years.

The British fine chemical industry—as we now understand it—had to be initiated under war-time *i.e.*, the worst possible conditons. The early post-war period afforded manufacturers the first opportunity to stabilise their immature efforts, but it was then that they experienced to the full the difficulties of obtaining plant and erecting buildings, long delays and high prices being the prominent features. The efforts of the industry—a new one— to expand were hindered by the dead weight of the excess profits duty. Yet, despite all the enormous difficulties, progress on the whole was really good until the Sankey judgment, like a bombshell, completely changed the situation. This, helped by the anomalous position of foreign exchanges, has led to the swamping of the market with German goods, a combination of circumstances which threatens defeat unless the Government steps in promptly and redeems its pledge to protect "key" industries.

Fine chemical manufacturers after very full consideration, have unanimously pronounced in favour of prohibiting imports of fine chemicals except under a system of licences, which should readily be granted when British manufacturers are unable to meet genuine demands for essential products. This, it will be seen, is precisely similar to the course it is proposed to adopt in the case of dyes: a natural coincidence when it is borne in mind that the fine chemical industry and the dye industry are indissolubly linked together and must inevitably go hand-in-hand. Indeed, one of the less obvious, but by no means negligible, features of the fine chemical industry is that it elaborates the otherwise useless by-products of the dye industry, thereby giving employment to thousands of men. Incidentally, it affords a training ground for chemists, technical and industrial, which no other school can rival.

An amendment to the Dyestuffs (Import Regulation) Bill was designed to exclude from the provisions of the Act "synthetic organic products imported mainly for medicinal or surgical purposes." This attitude on the part of some of our legislators does not augur well for the safeguarding of the organic chemical industry, nor for the future of the Empire. It is, indeed, a very short-sighted policy which seeks to gain a small, problematical, and temporary reduction in the cost of a certain number of medicinal substances at the expense of losing an industry already half-established, and which if fully developed would make the nation permanently self-supporting in the production of curative agents. Moreover, the Bill provides for the importation under licence of substances which cannot be produced at home. It is this kind of opposition, born in ignorance and nourished in apathy, which confronts those who have the national welfare at heart. It is to be feared that there are others remaining in the background and doing their work covertly, who are directly concerned that England shall *not* have a fine chemical industry, and who are doing all in their power to let her sink back to her pre-war dependence upon Germany.

The many uses of fine chemicals in peace time, which justify so fully the claim of the industry to be regarded as a "key" industry, do not need to be laboured here. Research chemicals for our universities and teaching institutions, together with analytcal reagents for the same purposes and for works' laboratories, have already been mentioned. The importance of the industry to medicine and national health is not confined to the supply of synthetic drugs, but rests also upon the fact that the expansion of an organic chemical industry is intimately associated with developments in biochemistry and in the most modern methods of treating and preventing disease.

It cannot be too frequently nor too cogently insisted upon that the nation which possesses fine chemical and dye industries possesses potential arsenals for waging war, so that the nation which does not possess them is ever at the mercy of nations which do.

The present critical position of the fine chemical industry is largely due to the lack of confidence which manufacturers have in the Government. To-day it is not too late to save the situation; soon it will be.—*Journal of Society of Chemical Industry*, December 31, 1920.

## PROCEEDINGS OF SOCIETIES.

### FARADAY SOCIETY.

*Monday, December 13, 1920.*

SIR ROBERT HADFIELD, Bart., F.R.S., President, was in the Chair.

DR. A. E. OXLEY communicated and initiated discussion on a paper presented by Prof. E. D. CAMPBELL (University of Michigan), entitled, "*A Force Field Dissociation Theory of Solution Applied to Some Properties of Steel.*"

The author considers that understanding of the properties of alloys has been obscured by the use of the term "solid solution" and by expressing constitution in terms of percentage weights. There is no essential difference between a liquid and a solid solution, and the constitution of both should be expressed as molecular or atomic concentrations per unit volume.

The electrolytic dissociation theory in its usual form is inapplicable to alloys. The force field force field theory, however, put forward simultaneously by Baly and the author is a modified form of it which is applicable to liquid and solid solutions alike. The assumption is made that in a molecule the electromagnetic force field associated with the constituent atoms is closed in the combination but in solution this force field is more or less opened out by the solvent, to an extent depending on concentration and composition. The reactivity of ions is due to the open force fields and not to the presence of electric charges. In the presence of an impressed e.m.f. the resultant of the reactivity is electrical resistance in the case of metallic solutions, electrical conductance in aqueous solutions.

Dr. A. E. OXLEY considered that the field force theory alone was insufficient to account for the

properties of solutions, the conceptions of Arrhenius were also required, otherwise Bragg's lattice structure did not apply. The union of two like atoms to form a molecule required that the electrons should be in ring or vortex motion or otherwise act as a magnetic unit or magneton. The Rutherford-Bohr, or "solar-system," atom did not explain the diamagnetic or paramagnetic properties of matter. Dr. Oxley went on to explain Langmuir's cube theory of atomic structure. His own theory might be supplementary to that if Langmuir's stationary electrons were made to describe a small orbit or be vortical in character.

The CHAIRMAN hoped Dr. Oxley's theory would prove to explain the remarkable magnetic properties of alloy steels and the phenomena of hardening.

Dr. OXLEY, in reply to a question, thought his conception could be made to fit in with spectral phenomena.

*"The Electrical Resistivity of Dilute Metallic Solutions."* By A. L. NORBURY, M.Sc.

It is well known that the small quantities of imprities in solid solution cause a large increase in the electrical resistvity of a pure metal. Data are collected showing the relative atomic effects of such impurities and a certain relationship appears to be brought out by doing so. The paper is divided into three sections.

*Section I.*

The general theoretic interpretation of data obtained by measuring the electrical resistivity of alloys is discussed.

(*a*) In the case of duplex alloys in which the componet metals are mutually insoluble and crystallise sde by side each crystal grain may be considered as a separate conductor. In so far as the arrangement of the grans tend to be in the nature of conductors arranged in parallel the conductivity will be a linear function of the composition. In so far as they tend to be arranged in series the resistivity will tend to be a linear function of the composition.

(*b*) In the case of alloys which form a continuous series of solid solutions the atomic effects of the metals on one another are approximately represented by the initial slopes of the observed curves on either side.

(*c*) Reasons are given for thinking that the initial additions of solute normally cause a linear increase in the resistivity of the metallic solvent.

(*d*) Temperature seems to affect the resistivity of solid solutions as if it were made up of two independent quantities of which the increased resistivity—consequent on solid solution formation—is very little influenced.

(*e*) Cold-work and variations in grain size have relatively small influences on the resistivity in the case of pure metals. In the case of duplex alloys the grain size has an increasingly large influence as the number of atoms forming the crystal boundaries becomes comparable with the total number of atoms present. The fall in resistivity consequent on tempering martensitic steel is discussed. It is suggested that in martensite the carbon is present in a highly dispersed condition, but is not in true solid solution in the α-iron.

*Section II.*

Data are collected showing the effects of various elements on the electrical resistivities of iron, nickel, palladium, platinum, copper, silver, gold, magnesium, cadmium, sodium, and potassium. The atomic effects of the solutes are plotted against the positions in the Periodic Table—the results bring out the general relationship that the atomic effect of a solute on the resistivity of a metallic solvent is large or small according as the solute is far from or near to the solvent in the Periodic Table.

*Section III.*

In this section the results are discussed.

(*a*) A comparison with the atomic volumes, intrinsic pressures, electrical resistivities, thermoelectric properties and decomposition potentials of the elements concerned shows that none of these atomic properties can be directly applied to explain the results. It is suggested that the atomic effects are small when there is little electrical attraction between the atoms of solute and solvent and large according as the electrical atraction between the two is greater.

(*b*) It seems probable that in the dilute solutions quoted the atoms of solute are not associated.

(*c*) Assuming, for example, the face-centred cube lattice in a dilute solid solution, a natom of solute will be surrounded by twelve equidistant atoms of solvent and will not be attached to any one of these atoms in particular. It will, therefore, exert attractive forces on the electrons of the surrounding atoms.

(*d*) It is generally assumed that metals conduct the electric current by means of their "free" electrons, the presence, therefore, of forces restraining the "free" electrons in solid solutions will account for their diminished conductivity.

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*Annual General Meeting, December* 13, 1920.

The following Officers and Council were elected to serve for the coming year:—

*President*—Prof. Alfred W. Porter, F.R.S.

*Past-Presidents*—James Swinburne, F.R.S., Sir Richard Glazebrook, K.C.B., F.R.S., Sir Robert Hadfield, Bart., F.R.S

*Vice-Presidents*—W. R. Cooper, Prof. C. H. Desch, Dr. J. A. Harker, O.B.E., F.R.S., Emil Hatschek, Prof. T. M. Lowry, C.B.E., F.R.S., Dr. E. H. Rayner, Dr. G. Senter.

*Treasurer*—Robert L. Mond, R.R.S.E.

*Council*—Dr A. J. Allmand, Dr. H. Borns, Prof. W. C. McC. Lewis, Harold Moore, O.B.E., Prof. J. R. Partington, C. C. Paterson, O.B.E., Prof. A. O. Rankine, Sir Robert Robertson, F.R.S., Sir T. Kirke Rose, Dr. W. Rosenhain, F.R.S.

In proposing a vote of thanks to the retiring President, Sir Robert Hadfield, who had guided the Society during the whole critical period of the war, Prof. Porter referred to the growth that had taken place in the Society's work and in its prestige during that period. He remarked that of the twenty-six General Discussions that had been organised by the Society, many of them in cooperation with other societies whose collaboration was greatly appreciated, no less than nineteen had been held during Sir Robert Hadfield's presidency.

# CORRESPONDENCE.

## THE PEOPLE'S UNION FOR ECONOMY.

*To the Editor of the Chemical News.*

SIR,—On July 16 last we wrote a letter on the extreme gravity of the financial position of this country, which you were good enough to publish. We were glad to observe the gradual awakening of interest in this matter, and the attention which all sections of the community are beginning to pay to the critical state of affairs. In order to promote further the views we expressed in July last the People's Union for Economy have now established their headquarters at 1, King's Buildings, Millbank, Westminster, S.W.1.

The People's Union for Economy will aim at keeping a watchful eye upon all Government expenditure with a view to directing attention to overlapping and waste in the administrative sphere. For this purpose it will operate through a strong Parliamentary Committee including members of all parties and of both Houses of Parliament, and they will seek to co-operate with other Associations working for the same objects. The Central Office aims further at becoming a bureau of information where all Parliamentary papers and estimates will be critically examined and filed for reference. It will be in constant touch with commercial and industrial bodies, individual economists and others in all parts of the country, with a view to providing the best possible material for criticism.

It is obvious that an organisation of this kind, which we believe to be without parallel in the country, must rely for its development upon the support of the public, whose interest it is solely designed to serve. We therefore invite all those who agree with the views we have expressed to give us their support by joining the Union, and by supplying reliable information of any instances of public waste and extravagance.

Forms of membership may be obtained on application to the Hon. Secretary, Mr. Leslie Hore-Belisha, 1, King's Buildings, Millbank, S.W.1.—

We are, &c.,

| | |
|---|---|
| SALISBURY | C. W. BOWERMAN |
| ASKWITH | J. W. WILSON |
| MIDLETON | RICHARD A. COOPER |
| EMMOTT | F. D. ACLAND |
| OSWALD MOSLEY | WALTER LEAF |
| GODFREY LOCKER-LAMPSON | LESLIE HORE-BELISHA |
| ISLINGTON | |

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Mr. ERIC TOMKINSON makes the following addition to his letter on "The Colour of Water' inserted in last week's issue :—

"It should be remembered that the molecular formula of water, determined from surface tension measurements, was found by Ramsay and Shields (*Zeit. physikal Chem.*, 1893, xii., 464; *Journ. Chem. Soc.*, 1893, lxiii., 1089) to be $(H_2O)_4$ at 0°."

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HALOGEN DERIVATIVES OF LEAD AND THALLIUM —They should, it appears, form well defined combinations. By varying the ratio of the two compounds in a mixture of Tl and Pb, in aqueous solution, M. Barlot successively isolated $PbBr_2$, TlBr, $PbI_3Tl$ and $TeClPbCl_2$.—*Comptes Rendus*, October 21, 1920.

# NOTES.

ROYAL INSTITUTION.—On Tuesday next (January 18), at three o'clock, Sir G. P. Lenox-Conyngham will give the first of two lectures at the Royal Institution on "The Progress of Geodesy in India"; on Thursday (January 20), Dr. Arthur Harden begins a course of two lectures on "Biochemistry (Vitamins)"; and on Saturday, January 22, Dr. P. C. Buck commences a course of three lectures on the "Madrigal: Rhythm—Key—Technique," with musical illustrations by the English Singers. The first Friday evening Discourse on January 21, will be delivered by Sir Frank Benson on "Shakespeare and Democracy"; and on January 28 by Sir James Dewar on "Cloudland Studies."

£20,000 FOR INDUSTRIAL HARMONY.—Of the many New Year honours conferred by His Majesty none was more deserved than the Baronetcy bestowed upon Col. Sir Wm. Dupree, J.P., D.L., who, early in the great war, foresaw that one of the greatest problems that would evolve from the conflict, and which would shake nations to their foundations, would be the question of relationship between employers and employed. Events that have happened in all countries of the world during the last twelve months have clearly proved the wisdom of Sir Wm. Dupree's judgment of what would be the trend in industrial matters. Serious though the situation has occasionally been in England, this country has happily been spared the terrors of civil strife, and it can with all deference be said of Sir Wm. Dupree, as of other like public-spirited men, that his broad-minded munificence and indefatigable energy have contributed materially to the factors which have enabled England as far to avoid the industrial rocks and snags on which she would undoubtedly have foundered. So keen was Sir Wm.. Dupree on what he felt to be his duty to his countrymen in this connection that in December, 1918, he approached the Rt. Hon. G. H. Roberts, M.P., who was then President of the Industrial League, and placed in his hands for the use of the League, and without any reservations whatever, a cheque for £20,000.

THE ACTION OF COPPER ON MOULDS.—The existing opinion in favour of the employment of anticryptogamic bouillies is based upon the theories of Millardet applied to hydrated copper oxide. Continuing the studies already submitted to the Academy, M. and Mme. Villedieu demonstrate that the metal Cu is not more toxic for Peronospoaceœ than for moulds, and that vine stocks are not protected against mildew, although sufficiently bathed with ammoniacal nitrate to find the metal in the ash from tissue of the leaves. Thus it seems possible to replace copper in the mixtures hitherto employed by some less expensive elements.—*Comptes Rendus*, October 18, 1920.

ACTION OF SELENIUM ON MOULDS.—The experiments of Messrs. Nemec and Varchav Kàs related to various varieties of *Mucdineœ* sown in a Raulin liquid modified according to their specific needs and mixed with seleniate of sodium. The influence of Se was especially notable with *P. Roqueforti*, but in the case *P. Candidum*, the metal apparently becomes toxic when the percentage exceeds a certain limit.—*Comptes Rendus*, October 18, 1920.

TRACES OF BROMINE.—The reaction proposed in 1912 by Messrs. Denigès and Chelle, according to the indications of Lebeau, is somewhat modified by M. Damiens, and sensitiveness becomes such that by a simple colorimetric method, after oxidation of iodine in form of iodic acid, it attains 1/6,000,000.—*Comptes Rendus*, October 20, 1920.

## New Patents.

THIS List is specially compiled for the *Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, W.C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

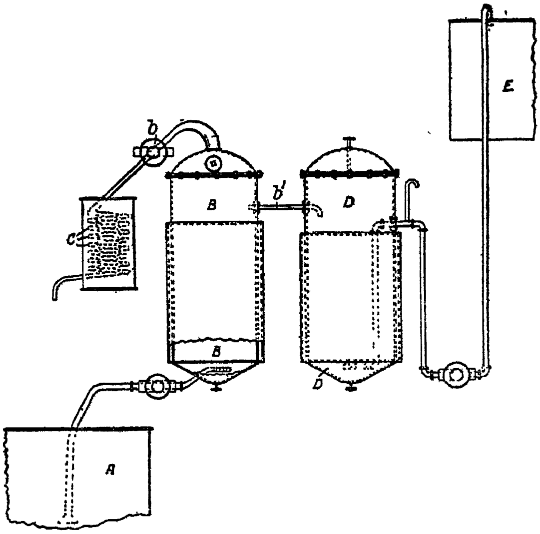
35853—Fyfe, A. W.—Manufacture of 1 chlor-2-amino-anthraquinone Dec. 21st.
35876—Rollason, A.—Production of Ammonia. Dec. 22nd.
36081—Starrels, J.—Process for producing fatty acids of high melting point. Dec. 23rd.
35970—Stockholms Superfosfat Fabriks Aktiebolag—Method of Manufacturing acetaldehyde from acetylene. Dec. 22nd

*Specifications Published this Month.*

155318—Rollason, A.—Production of ammonia.
155319—Moore, T. S.—Reduction of substituted nitro compounds, nitroso, and azo compounds.
155373—Arrowsmith, H. T.—Manufacture of acid pots to be employed in the production of white lead.
148579—Sudfeldt & Co.—Process for obtaining the salts of sulpho acids and alkyl-sulphuric acids from acid resins.

*Abstract Published this Week.*

Mr C. J. Robins of Hull has obtained a Patent for means and apparatus for recovering the acetic acid, methyl alcohol, and acetone formed by the destructive distillation of wood in suction gas plants, No. 152420 The wash-water from the suction gas scrubbers



is passed over chalk or barium carbonate until a sufficient concentration of acetate is obtained, and at the same time the methyl alcohol and acetone are withdrawn by means of vacuum. The wash-water contained in the tank A is pumped into the vessel B, provided with a heating jacket, where it passes through lumps of calcium or barium carbonate, and overflows through the pipe b1 into the vessel D, which also contains calcium or barium carbonate and is fitted with a cooling jacket. The methyl alcohol and acetone are drawn off from the heated wash-water in the vessel B by means of the pump b into the condensing coil C. The liquid issuing from the vessel D is pumped into the tank E, from which it can be run back to the scrubbers of the suction gas plant. The process is repeated until the content of calcium or barium acetate is sufficient to justify its recovery by evaporation.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and forward on post free for the official price of 1/- each.

## MEETINGS FOR THE WEEK.

*Monday, January 17, 1921.*

Royal Society of Arts, 8. "Aero Engines," by Alan E. L Chorlton.

*Tuesday, January 18.*

Royal Institution, 3. "The Progress of Geodesy in India," by Col. Sir Gerald P. Lenox-Conyngham.
Society of Chemical Industry. (At Edinburgh).
Mineralogical Society, 5.30. "The Olivine Group," by A. F. Hallimond. "A method of rock-analysis diagrams based on statistics," by W. A Richardson. "Identity of Trechmann's 'B-tin' with Stannous sulphide," by L. J. Spencer. "Linarite, Caledonite, and associated minerals from Cumberland," by G. F. Herbert Smith. "On the Adare and Ensisheim Meteorites," by G. T. Prior.
Institution of Petroleum Technologists, 5.30.

*Wednesday, January 19.*

Royal Society, 4.30. "The Magnetic Mechanical Analysis of Manganese Steel," by Sir Robert Hadfield, S. R. Williams and I. S. Bowen. "A selective hot Wire Microphone," by W. S. Tucker and E. T. Paris. "Siren Harmonics and a pure tone Siren," by E. A. Milne and R. H. Fowler. "On the Design of Diaphragms capable of continuous Tuning," by Prof. L. V. King.
Royal Society of Arts, 4.30. "The Future of Industrial Management," by F. M. Lawson.
Royal Microscopical Society, 8.

*Thursday, January 20.*

Royal Institution, 3. "Biochemistry (Vitamins)," by Dr. Arthur Harden.
Institution of Mining and Metallurgy, 5.30.
Chemical Society, 8.

*Friday, January 21.*

Royal Society of Arts, 4.30. "Indian Timbers," by R. S. Troup.
Royal Institution, 9. "Shakespeare and Democracy," by Sir Frank Benson.

*Saturday, January 22.*

Royal Institution, 3. "The Madrigal—(1) Rhythm," by Dr. Percy C. Buck.



## NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemical Apparatus, &c., for review or notice to be addressed to the EDITOR.

**SUBSCRIPTIONS,** £1 12s. per annum, payable in advance, should be addressed to the MANAGER.

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THE CHEMICAL NEWS,
97, SHOE LANE, LONDON, E.C.4.

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# THE CHEMICAL NEWS.

VOL. CXXII., No. 3171.

## THE STORING OF LIGHT.

### (A HISTORICAL REVIEW OF INORGANIC PHOSPHORESCENCE.)

By J. FREDERICK CORRIGAN.

NO department of history can offer a more peculiar and fascinating study than that which deals with the introduction of mankind to the natural phenomena, and which traces the early struggles and progress of a crude science founded on mystery and superstition, towards the elucidation of the problems of nature. The histories and legends of kings and princes, fair maidens and chivalrous knights, of fearsome monsters and enchantments give, it is true, a thrill of pleasurable excitement to the reader, but in all of them something is lacking—an undefinable something which is ever present in the romance of the eternal quest for truth. A romance, however, which under certain aspects is pathetic, tinged with sorrow and with blighted hopes; a story of the struggles of early man against darkness and mystery, and with the crude ineffective tools of his own forging. Every new idea, every newly-discovered fact is an additional step forward along the lonely tortuous road which marks the path of science. But at what cost is each advance made? At the expense of almost Herculean effort, heroic self-sacrifice, and untiring devotion.

Phosphorescence, as a natural phenomenon, is widespread. It occurs in various guises, both in the living and in the mineral world. Its first introduction to mankind would most probably take place in the remote age when some poor rude uncivilised man was first frightened out of his wits on noticing the luminous appearance of decaying animal matter. This phenomenon he would ascribe to the "soul" of the animal rising forth to reveal itself to him, and subsequently luminescence would always be associated with the supernatural.* A phosphorescent object would be regarded as being

"Luminous, gemlike, ghostlike, deathlike."†

In the same way, the first prehistoric savage, who, on dipping the oar of his primitive canoe into the placid tropical waters and finding that it emerged irridescent, shining with a pale ghostly light, would doubtless have had the phenomenon of phosphorescence very forcibly impressed upon him. And then, as time went on, luminous flying-insects and beetles would be noticed, although as yet fire would be an unheard-of thing. Needless to say, these insects would be invested with a soul and would be preserved as sacred.

This is borne out by the fact that the earliest records of phosphorescence occur in the early Eastern manuscripts, where reference is made to the sacred insects of the Temple, which in the darkness shone with a light of their own. Biblical allusions to gems which shine in the dark may also occasionally found.

* Even at the present time, "apparitions" are invariably associated with luminous phenomena.

† Tennyson: "Maud."

Pliny was acquainted with the luminous appearance of decaying animal and vegetable matter. He also refers to certain precious stones which shine in the dark. It is customarily supposed, however, that apart from these few observations of Pliny, the phenomenon of phosphorescence did not attract much attention until the mediæval discoveries of the various "phosphoruses." It is more probable that the 16-17th century discoveries of the phosphorescent alkaline-earth sulphides were merely *rediscoveries* of facts known long before the Christian era. Such circumstances are not wholly unknown to science.

A strong point in favour of this view is found in Berthelot's discovery in certain 13th and 15th century manuscripts of various translations of Greek alchemical writings. Amongst them, Berthelot found recipes explaining methods of "colouring artificial precious stones, emeralds, carbuncles, hyacinths, according to the book taken from the shrine of the Temple." The authority of several alchemical writers is quoted, including Agathodemon, Democritus, and Ostanes, and a close study of the writings leaves no doubt as to the acquaintance of the ancients with methods by which stones could be rendered phosphorescent simply by coating them with a thin layer of a substance already phosphorescent.

Further evidence may be also obtained from Livy (xxxix., 13): "Matronas Baccharium cum ardentibus facibus decunise ad Tiberium demissoque in aquam faces, quia vivum sulphur cum calce insit intergra flamma efferre."

Which, with a certain ease of translation, may be rendered: "The Bacchantes would run down to the Tiber with burning torches, and plunging them into the water, would take them out with the flame unextinguished because they were covered with a mixture of living lime and sulphur."

Thus it is apparent that even the phosphorescence of calcium sulphide was known centuries before it was "discovered" by Marggraf in 1750.

Passing rapidly over a gap of nearly a thousand years, during which time the knowledge of phosphorescent substances appears to have been completely lost, we find at the beginning of the 16th century, Benvenuto Cellini in his "Art of Jewellery" putting on record the fact that some precious stones had been observed to shine in the dark; also the observation of Albertus Magnus, that diamonds when moderately heated, became luminous.

However, the first discovery which attracted the then rising scientific attention was that of Vincenzo Cascariolo, a cobbler of Bologna, who, in 1639 (according to some authorities, 1602) noticed that when a particular kind of earth found in the neighbourhood was heated in a certain manner, it acquired the remarkable property of emitting a soft, ghostly light after a certain amount of exposure to the rays of the sun. This substance was called by its discoverer *lapis solaris*, and on account of its power of attracting and storing up the golden rays of the sun, it was considered by Cascariolo to be nothing less than the long sought for Philosopher's Stone. The *Bologna Stone* was treated as a discovery of the greatest import. Learned treatises where written on the subject by the philosophers of the day, amongst whom were F. Licetus, a professor of philosophy at Bologna,

Celias, Potterius, and Kircher. Frequent attempts at its chemical analysis were made; speculations as to its nature and origin were entertained, but with little success. Science was not yet sufficiently free from the fetters of alchemy to enable any real progress to be made.

About this time (1609), Brandt of Hamburg had discovered phosphorus, by distilling a mixture of concentrated urine and sand, at a red heat. Being the possessor of business instincts as well as of alchemical attainments, he jealously guarded the secret of the preparation of the *Phosphorus Mirabilis*, and it was only after some time that he sold the secret to Krafft for a considerable sum of money. Krafft brought the phosphorus over to England, where the specimens exhibited created an enormous sensation. A new zest was added to the production of phosphorescent bodies, and the secret of the preparation of *Brandt's Phosphorus* was much sought for. Eventually, however, Kunkel (1678) and Boyle (1680) succeeded in effecting a preparation by means of methods similar to that of Brandt.

Boyle was also attracted to the study of other forms of phosphorescence. He had observed that diamonds gave out light when heated or rubbed, and in 1663 he investigated the phenomenon of the phosphorescence of decaying organic matter. Beccarius also made a searching examination of various substances, and he claimed to have found that "almost everything in nature imbibes more or less light, and emits it again in the dark." He divided bodies into several classes as they were phosphorescent "with or without preparation." Almost all vegetable and animal substances, when perfectly dry, he considered to possess this property, which was particularly well exhibited in the case of paper.

In 1677, G. A. Baldwin, of Misnia, whilst engaged in a search for the Philosopher's Stone, discovered that the product obtained by dissolving chalk in nitric acid, shone brightly in the dark, after exposure to sunlight for a few minutes. Great interest was again aroused by this discovery, and Baldwin, who was formerly a bailiff, found himself suddenly raised to the rank of an honoured philosopher. In a letter to the Royal Society (*Phil. Trans.*, 1676, ii.), he says: "This phosphorus contains the real spark, yea the most secret soul of the fire and light of nature, and consequently the innate and invisible fire of the philosophers; attracting magnetically the visible fire of the sun, and afterwards emitting and diffusing in the dark, the splendour of the same."

The discovery of Baldwin's phosphorus was particularly welcome, as the preparation of the Bolognian stone had been kept more or less secret. The new discovery, however, threw some light on the matter, and it was followed some little time afterwards (1764) by the discovery of *Canton's phosphorus*. Canton prepared his phosphorus by calcining oyster shells with sulphur, and it is to his credit that he was really the first who attempted to systematically investigate the phenomenon. He found that the phosphorus could be made to shine by heating it, after its spontaneous phosphorescence had ceased. He devised experiments whereby the intensity of the light which excited the phosphorescence could be compared, and he also noted that the phosphorescence took place equally readily under alcohol or ether, but that water appeared to have some action on the substance.

On the analysis of Bologna-stone and its identification as a sulphide of barium by Marggraf (1750), and because of the progressively increasing scientific methods displayed in investigating the phenomenon, the preparation of phosphorescent substances became more frequent, and many were the uses to which these bodies were put. *Homberg's phosphorus* ($CaCl_2$) was sold in phials and used for illuminating the dials of watches and timepieces in the dark. Celestial objects, such as Saturn and his ring,* the phases of the moon, &c., were represented by cutting the object in wood and smearing the surface of it with a paste composed of equal parts of the white of an egg, and (Canton's Phosphorus) (Priestley's "History of Light and Colours," 1772).

In addition to the phosphorescence of the alkaline-earth sulphides, by means of which the sun's rays were seemingly absorbed and stored up, other types of phosphorescence began to be discovered. Reference has already been made to Boyle's observations on the phosphorescence of diamonds when heated or rubbed. In 1705, Francis Hawkesbee observed that friction between two glass surfaces "in common air, in the vacuum of an air pump, or under water" produced "a very considerable light." Du Fay noticed that some substances "shone with unusual splendour while they were dissolving, and thereby heated, in water: but this did not continue long." D. Hoffman discovered that certain felspars were luminous when rubbed together, and Pott added flints, certain crystals, and porcelain to the list of substances which gave out light when rubbed. Thomas Wedgwood, however, is generally credited with the discovery of "Luminosity by Attrition." In an extended paper on "The Production of Light from Different Bodies, by Heat and Attrition (*Phil. Trans.*, xvii., 128, 215), he separated substances into:—

(*a*) Bodies giving out light on warming.
(*b*) Bodies evolving light on attrition.

With regard to the former class, he found that the substances were by far the most luminous when they were first heated; that the duration of the light produced varies to a large degree, in some cases being almost momentary, and in others lasting for several minutes. Bodies of the latter class he found to be only luminous when rubbed. As soon as the rubbing was discontinued, the luminescence disappeared. Wedgwood was also the first to point out the yet unexplained fact that bodies emit a peculiar odour on attrition. He found it to be most persistent when the friction was greatest, and also to be independent of the light produced, as it was often present when the light emitted was practically nil.

But here we must draw a close to this brief sketch of luminescence throughout the ages. After the time of Wedgwood, the chain of observations and discoveries, never markedly coherent, becomes hopelessly broken and entangled in the oncoming tide of the scientific revolution which began about this period. In conclusion, however, a few remarks on the early theories of phosphorescence may be opportune.

Evelyn in his "Diary" (1650) refers to phosphorescent powders and preparations as a means

* Only one ring was known at this period.

of "bottling up sunlight." This observation, probably given out with cynical intent, contains the gist of most of the early theories, and even now there remains much to be said in favour of it. Phosphorescent substances or "light magnets" as they were often called were considered to act as veritable *light-accumulators*, rapidly absorbing light, and afterwards emitting it gradually when placed in the dark. Priestley, in his "History of Light and Colours," says: "The hypothesis of the materiality of light is peculiarly agreeable to the phenomena of the Bolognian Stone, which has the remarkable property of imbibing light, of retaining it for some time, and of emitting it again; and more especally by its emitting it more copiously according to the degree of heat applied to it."

Not all the early experimenters agreed with this type of theory. On the other hand, Kircher put forward a theory in which he supposed that the air "abounds with a subtle vapour which is very easily illuminated." The phosphorescent substance absorbed this vapour (and presumably the illumination also) and gradually evolved it in the dark. But the theory of Kircher and similar ones however, were regarded as fantasies, and only the speculations based on the material nature of light made any progress—that is, if chemical theories *did* progress at all, in those days.

It is not within the scope of this article to enter into the modern theories of luminescence. Suffice it to say that they are all highly problematical and delightfully at variance with one another. Probably, however, in view of the modern tendency towards a material or semi-material conception of light and heat we may witness at some not long-distant date the absorption of all these varying and antagonistic hypotheses into one general, revived, and modified theory of *The Storing of Light.*

## THE CHEMISTRY AND CRYSTALLOGRAPHY OF SOME FLUORIDES OF COBALT, NICKEL, MANGANESE AND COPPER.*

By FLOYD H. EDMINSTER and HERMON C. COOPER.

### *Introduction.*

THE fluorides of the bivalent heavy metals such as cobalt, nickel, and copper, have never been fully investigated, neither have their composition and crystalline forms, including isomorphous relations, been satisfactorily established. An examination of the description of these compounds in the handbooks (*e.g.*, "Gmelin-Kraut") leaves one in doubt as to the facts and relationship.

In 1824 Berzelius (Berzelius, *Pogg. Ann.*, I., 1824, p. 28; *Ann. chim. phys.*, [2] 1823, xxiv., 61) prepared the fluorides of cobalt, nickel, and copper, and regarded them as so similar that he described them together. "If the carbonate (of the metal) is treated with hydrofluoric acid, it will dissolve with effervescence, but soon a salt is precipitated as a heavy powder. If more and more of the carbonate be added, the effervescence continues, but the salt already formed decomposes, especially if warmed, and there results a pulverulent basic salt. If the addition and decomposition of the carbonate be stopped before this salt (powder) forms and the solution be evaporated, there separates out a crystalline crust. . . . In this process there is given off the excess of acid which the dissolved salt contains. If the crystallised salt be covered with a very small amount of water and the mixture be allowed to stand for a long time at room temperature, there results a saturated solution which will deposit these same crystals on evaporation. If, however, the mixture is heated to boiling with much water, decomposition occurs, part of the salt dissolving in the liberated acid and another part remaining undissolved as a basic salt."

Berzelius selected the copper salt foi anlysis, and found that on heating it with lead oxide there were given off two molecules of water, not in the least acid. The green pulverent salt resulting from the decomposition of the neutra lsalt by boiling water proved, by the same method of analysis, to be basic salt of the formula $CuO.CuF_2.H_2O$.

The three metals, cobalt, nickel, and copper, were thus regarded by Berzelius as forming entirely analogous fluorides; a crystallised normal fluoride, $MF_2.H_2O$, and an amorphous basic fluoride.

About fifty years later, F. W. Clarke (Clarke, *Am. Chem. Journ.*, 1887, xiii., 290) described the preparation of a supposedly new fluoride, made by evaporating a solution of nickel hydroxide in hydrofluoric acid, whereby a crystalline crust is formed. The analysis of this crust gave the formula, $NiF_2.3H_2O$.

In 1884, Balbaino (Balbaino, *J. Chem. Soc.*, 1884, ii., 1264) stated that he prepared the hydrated cupric fluoride ($CuF_2.2H_2O$) of Berzelius by dissolving copper carbonate in hydrofluoric acid and adding 95 per cent alcohol, which precipitated a pale blue crystalline powder.

Poulenc (Poulenc, *Compt. Rend.*, 1892, cxiv., 1426; *Ann. chim. phys.*, [7] 1894, ii., 47; *Ber.*, 1892, xxv., R. 662) is credited with the first description of the anhydrous fluorides. They are only of incidental interest to us here, but it may be noted that, according to Poulenc, the anhydrous nickel fluoride is formed as an amorphous yellow powder or as green crystallised prisms The anhydrous cobalt fluoride is either a rose-red amorphous powder or red prismatic crystal.

In 1905, Böhm (Böhm, *Z. anorg. Chem.*, 1905, xliii., 330) reviewed the work on the fluorides of the heavy metals, called attention to the lack of accurate inevstigations of well-crystallised material, and prepared, along with several other complex fluorides, the acid fluorides of cobalt, nickel, and copper. He stated merely that he obtained these by dissolving the freshly precipitated hydroxides or carbonates of the metals in hydrofluoric acid and concentrating until crystals appeared. His cobalt and nickel fluorides are describe as, respectively, red and green prisms, having similar form and composition. They are stable in the air and easily soluble in water and dilute acids. The metal was determined by electrolysis from a sulphate solution, the fluorine by heating the salt with pure Iceland spar and the

*A more detailed account of this work was submitted to the Faculty of the Graduate School of Syracuse University by Floyd H. Edminster in May, 1918, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

water by heating a mixture of the salt with lead chromate in a combustion tube. Böhm found the copper-fluoride crystals to be different from the others in that they soon lose their water of crystallation in the air and that they decompose completely when heated in a closed tube, water and hydrogen fluoride escaping, while copper oxide remains. In the case of copper fluoride the fluorine was determined by neutralising with an excess of sodium hydroxide and titrating back with standard hydrochloric acid. The formulas assigned by Bohm for these fluorides are of a strongly acid fluoride type.

*Purpose of the Investigation.*

It is hardly possible that the conclusions of Berzelius, Clarke, and Böhm can all be correct, since all of them offer different formulas for salts prepared by methods which should yield the same type of fluoride for a single metal. It is reasonable to suspect that the old master, Berzelius, drew too hasty conclusions from his brief experiments.

Notwithstanding the slight experimental foundation on which the existence of the normal fluorides is based, one is inclined to prefer a normal salt formula to an acid salt formula for a halide obtained from the hydroxide or carbonate and acid, because it is in this way that the most familiar normal chlorides and bromides are prepared.

We have undertaken a combined chemical and crystallographic study of these fluorides, not merely to ascertain the facts in question, but to see whether an isomorphous series is involved.

*Preparation of Materials.*

The following general methods were investigated. (1) Treating the hydroxide of the metal with an excess of hydrofluoric acid. The excess is necessary for avoiding the formation of the basic salt. (2) Decomposing the carbonate with hydrofluoric acid. In either of these cases the resulting solution is evaporated until crystals appear. Both methods yield satisfactory results. (3) "Dissolving" the metal in hydrofluoric acid. In most cases the action was so slow that only a very small concentration could be obtained. (4) Treating a salt of the metal (the acetate) with hydrofluoric acid. (5) Double decomposition of an alkali fluoride and a salt of the metal. A complex fluoride resulted.

The first general method was ordinarily employed. The hydroxides were precipitated from the acetate solution with sodium hydroxide, the precipitate being washed repeatedly by decantation with cold water and finally with hot water, until the filtrate gave no colour with phenolphthalein. The washing must be very thorough, since the gelatinous hydroxide adsorbs the alkali greedily. An excess of alkali was avoided and the precipitate was heated in an excess of water to boiling repeatedly before bringing it upon the filter. The moist hydroxide was then dissolved in C. P. hydrofluoric acid in a platinum basin and the solution was filtered through a wax funnel into a wax bottle, from which it was taken as needed.

Böhm specifies that the solution should be evaporated in a vacuum dessicator over sulphuric acid until crystals appear. Attempts to follow this procedure resulted in the formation, not of crystals, but of a crystalline crust on the sides and bottom of the container and an arborescent creeping growth extending often over the sides of the vessel. The walls of the container and the dessicator were bedewed with a strongly acid solution, which was not absorbed by the sulphuric acid. If the evaporation took place in the open air, the crust was drier and harder and more difficultly soluble.

Under the microscope this crust looked different according to the conditions under which the evaporation took place. In some cases the crust was only a mass of nodules, while in others it appeared to be a mixture of amorphous material and of small but fairly definite crystals. In the case of copper the crust was, fortunately, almost wholly crystalline.

In view of the fact that the anlyses of Berzelius and Clarke were made on material prepared in this way, special attention was given to preparing a product which could be regarded as suitable for analysis, but examination with the petrographic microscope showed the preparations—except in the case of the copper salt—to be either amorphous and of indefinite water content or mixtures of amorphous and crystalline material. Analses of these products were made and indicated roughly a ratio of cobalt or nickel to fluorine of 1 : 2, but the character of the crystals was too indefinite to warrant careful investigation of their composition.

*Recrystallisation.*—If this crust is placed in about an equal weight of water, the crystalline portion can be seen to dissolve out, while the amorphous portion remains. If the amount of water is increased and the temperature raised, all of the material dissolves. Except in the case of cobalt no well-defined crystals, capable of measurement, were obtained from the original solution of the hydroxide in hydrofluoric acid. All of the crystals used for analysis and measurement have been obtained from the water extract of the crystalline crust, the extract being allowed to evaporate slowly in the air. Even then some of the crust is nearly always formed around the crystals and a second recrystallisation is necessary to free them entirely from the crust. Each recrystallisation reduces the acid concentration until in the third is practically negligible.

We hesitated to recrystallise from pure water because of the possibility of hydrolysis and, particularly, because of the possible loss of acid in case the salts should be acid fluorides, as our investigation as well as Böhm's disclosed. Contrary to expectations, the proportion of amorphous material lessened, rather than increased, with decreasing acidity, indicating that it is not a basic salt. The acid concentration, however, appears to control the equilibrium involving the crystal and amorphous phases.

*Preparation of Cobalt Fluoride.*—Our first preparation of cobalt fluoride was by treating the hydroxide with hydrofluoric acid. Because of the tendency of the cobalt (ous) hydroxide to oxidise in the air during the long washing process to cobaltic hydroxide, wihch is insoluble in hydrfluoric acid, we generally used the carbonate instead. It is permanent in the air, filters more quickly and is more easily washed. It is, however, less soluble than the cobaltous hydroxide. To be sure, the carbonate, when added to the

hydrofluoric acid, is decomposed as long as there is any acid present, but, as Berzelius stated, there is precipitated a fine rose-red powder, which is dissolved only upon the addition of more acid and water.

The original solution was evaporated on a water-bath until solid appeared, whereupon it was removed to a heat-insulated box of the Swedish box, or fireless cooker type, and allowed to cool slowly. No crystals formed. Even after standing in the box until half of it had evaporated, the solution continued to yield a brittle crystalline crust, the last portion being the same as the first.

The next trial was made in the open air, using the mother liquor from this crust, but no real crystals were obtained. The same method was tried, starting with a dilute solution and allowing it to evaporate slowly at an even temperature, with no better results. Bohm's method of letting stand in an evacuated dessicator over sulphuric acid was then tried. The evaporation proceeded slowly because, as stated above, the escaping vapour was not absorbed by the sulphuric acid but condensed upon the inner wall of the dessicator. Solid fluoride formed upon the sides of the basin and then crept over the edge. Under the microscope this crust appeared to have no crystal form and no definite composition.

The cobalt fluoride crust, however formed, is slowly soluble in very dilute hydrofluoric acid. For this reason a few drops of hydrofluoric acid were added to the water on dissolving. Upon evaporation the same results were obtained as in the first evaporation. Since the crust appeared to consist of more than one form of material, differing in solubility, a comparatively large amount was treated with a small quantity of water and warmed. The filtered solution upon standing for six hous began to deposit crystals which, though accompanied by crust, were sufficiently distinct from it to be separated mechanically. When these crystals were recrystallised from slightly acid water, very clean, well-defined crystals were obtained.

*Preparation of Nickel Fluoride.*—For the preparation of nickel fluoride either the hydroxide or the carbonate may be used, since the hydroxide, unlike that of cobalt, is stable in the air. The first product was a crystalline crust, as for cobalt. The crust forming on the surface of the evaporating solution is identical in appearance under the microscope with that deposited on the bottom. Satisfactory crystals were obtained in the same way as for cobalt, the cleanest ones resulting from a second recrystallisation from water.

*Preparation of Manganese Fluoride.*—Of all the fluorides investigated that of manganese is the most difficult to prepare. The hydroxide is less stable in the air than that of cobalt; so that, before it can be thoroughly washed, much of it has become insoluble in hydrofluoric acid; but a more serious difficulty is the comparatively slight solubility of the manganous hydroxide in hydrofluoric acid. The carbonate likewise dissolves only to about 10 per cent; further addition of the carbonate produces a marked effervescence and the precipitation of a fine powder, which does not dissolve upon the addition of more acid and water. The solution of the fluoride is consequently very dilute.

If the manganous fluoride solution be heated on the water-bath, the fluoride precipitates as the powder, so that all evaporation must be done at room temperatures, requiring on the average six weeks to produce crystals. The crust also forms as in the case of cobalt and nickel, but decomposes when digested with water. We attempted to obtain manganese fluoride by dissolving the metal in hydrofluoric acid, but obtained only manganese dioxide, which was formed by an unusually vigorous reaction between the metal and acid.

*Preparation of Copper Fluoride.*—For the preparation of copper fluoride the hydroxide is to be preferred to the carbonate, since the hydroxide reacts faster with hydrofluoric acid. Although it forms a basic salt upon standing in the air, the product is soluble in more acid. If the copper fluoride solution be evaporated slowly, small irregular blue crystals form on the bottom of the basin; while, if the evaporation takes place on the water-bath, the fluoride appears as a clear crystalline crust of constant composition. Both the small crystals and the crystalline crust were free from the granular, amorphous material so persistent in the deposition of cobalt and nickel fluorides. They were regarded as sufficiently well defined for analysis. The analyses showed the two products to be identical in composition, viz. to be a normal fluoride.

These normal fluoride crystals are difficultly soluble in water, a white coat forming upon the surface. If an excess of water is added and the solution is heated, the filtrate yields upon evaporation well-defined three- or sixsided prismatic crystals. These are very soluble in water and, strange to say, have the composition of an acid fluoride. On exposure to the air they effloresce rapidly. If they are heated, water and hydrogen fluoride are evolved, leaving copper oxide in the tube. Presumably the hydrogen fluoride is driven off first, whereupon the water of crystallisation hydrolyses the copper fluoride.

### *Observations on Dissociation.*

The crystal fluorides of cobalt, nickel, manganese, and copper all evolve hydrogen fluoride when exposed to the air. After a portion of one of these substances is washed and dried and set aside on the watch glass the latter is found to be etched in three minutes. The gradual loss of hydrogen fluoride is a very important property of these fluorides. It means that the compound cannot be preserved with certainty of its retaining its original composition and that analyses must be made with the freshest possible product. This phenomenon will be referred to the discussion of the analysis. It would be interesting to deter mine the rate or decomposition, but no work has been done upon it thus far.

The cystals are soluble in water and dilute acids. When heated, they give off water and hydrofluoric acid and are themselves converted to the oxides, as stated by Böhm, for the copper salt.

### *Analysis of the Fluorides.*

For the *metal* the following general methods are applicable. (1) precipitation as the hydroxide or sulphide with subsequent reduction in a stream of hydrogen; (2) evaporation with sulphuric acid

and weighing as the anhydrous sulphate; (3) heating at red heat to convert the fluoride into the oxide; (4) electrolytic deposition.

The *total fluorine* can be determined volumetrically by adding an excess of standard alkali and titrating back with standard acid. In this case the precipitated hydroxide is filtered off before the titration, else it will obscure the end-point. With nickel and copper, using phenolphthalein as an indicator, a very good end-point can be obtained if the alkali be added slowly to the warm solution until the free hydrofluoric acid is neutralised and the hydroxide of the metal is precipitated.

The gravimetric determination of fluorine is based upon its precipitation as an insoluble fluoride. A number of metals form insoluble fluorides, calcium being the one most commonly used. Lead chloride precipitates the fluorine as the double halide, PbFCl (G. Starck, *Z. anorg. Chem.*, 1911, lxx., 173; *J. Chem. Soc. Abs.*, 1911, c., ii., 436), and lithium chloride is said to give accurate results (Deladrier, *J. Chem. Soc.*, 1904, lxxxvi., 440). In our work with the fluorides lead chloride gave results uniformly low and lithium chloride failed in some cases to give a precipitate The difficulties of precipitation are well known. Calcium fluoride is an extremely finely divided, slimy precipitate, which passes through nearly all filters the first time. Refiltering through the same filter proved to be exceedingly tedious, and washing was impracticable because of the time consumed in filtration of the solution. However, a number of determinations for fluorine were made by precipitating it with calcium chloride or calcium acetate. While the results were not accurate, they afforded independent confirmation of those obtained by other methods so far as the interpretation was concerned.

The purpose of adding the carbonate to the fluoride in the calcium fluoride method (Berzelius) is to assist in the filtration. A modification of this procedure has given good results in our work. Instead of adding sodium carbonate we made the solution slightly acid with acetic acid. An amount of standard ammonium oxalate was then added so that the calcium oxalate precipitated would be approximately the same as the weight of calcium fluoride. The two precipitates were then filtered off together in a Gooch crucible, dried and weighed. The difference between the weight of the combined precipitate and the weight of the calcium oxalate, corresponding to the ammonium oxalate added, gave the calcium fluoride. The decided advantage lies in the elimination of the decomposition, and furthermore, it does not necessitate a second filtration. The calcium oxalate serves the same purpose as the calcium carbonate and does it equally well. None of the absorption methods was used in the analysis for fluorine.

The determination of *crystal hydrate water* is the most difficult, since a temperature sufficiently high to expel the last traces will cause a loss of at least a part of the hydrogen fluoride. The method used by Bohm—heating the fluoride with lead oxide—is the only one described as being satisfactory. In the analyses that follow the water determinations were so variable that they were used only as rough indications of the amount present. For calculating formulas use was made of the percentage of water by difference.

(To be continued.)

## THE MOLECULAR STATE OF WATER VAPOUR.*

By JAMES KENDALL.

Up to a few years ago it was universally considered that water vapour at ordinary temperatures was, so far as could be deduced from vapour density determinations, entirely monomolecular $H_2O$ and obeyed the gas laws within the limits of experimental error. Regnault's measurements gave 18·0 for the molecular weight, Gay-Lussac's 18·01 and Leduc's 18·1, while the formula $H_2O$ requires the value 18·016 (Abegg, "Handbuch der anorganischen Chemie," [1] 1908, ii., 67). In the derivation of equations for osmotic pressure, vapour pressure lowerings, &c., in dilute aqueous solutions, the assumption was accordingly made, without any question, that water vapour could be treated as a perfect gas. Some measurements by Winkelmann (Winkelmann, *Wied. Ann.*, 1880, ix., 208) appeared to indicate a tendency towards association at temperatures slightly above normal, but even as late as 1907, in a discussion at the Faraday Society (Wilsmore, *Trans. Faraday Soc.*, 1907, iii., 85) the different results quoted for saturated vapour at 15° varied more among themselves than from the theoretical value, and the conclusion that the vapour behaved as a perfect gas was undisputed.

In 1908, however, some calculations were published by Bose (Bose, *Z. Elektrochem.*, 1908, xiv., 269), based upon new vapour density determinations by Kornatz (Kornatz, *Inaug-Diss.*, Königsberg, 1908), claiming that association in the saturated vapour was considerable even at ordinary temperatures. The equilibrium $(H_2O)_2 \rightleftarrows 2H_2O$ was assumed to exist in the vapour phase and an equation for the variation in the equilibrium constant with temperature was derived. This equation indicated for the saturated vapour at 0°, 6·6 per cent association; at 50°, 8·2 per cent association; at 100°, 8·9 per cent association.

In 1915, Oddo (Oddo, *Gazz. chim. ital.*, [1] 1915, xlv., 319), evidently ignorant of the work of Bose, calculated from the tables of Landolt-Börnstein ("Tabellen," 1912, p. 369) (Regnault's data, reproduced from Zeuner's "Technische Thermodynamik") the molecular weight of saturated water vapour between —20° and 200°, obtaining values steadily increasing from 17·03 at —20° to 19·92 at 200°. Only at 32° did the experimental value agree with that required by monomolecular $H_2O$. The conclusion was drawn that at temperatures below 32° a *dissociation* equilibrium, $H_2O \rightleftarrows H^+ + OH^-$, existed, and above 32° an *association* equilibrium: $(H_2O)_2 \rightleftarrows 2H_2O$. At —20° the degree of "ionisation" was calculated to be 5·79 per cent; at 200° the "association" reached 19·11 per cent. Great emphasis was laid upon the former phenomenon—*the spontaneous ionisation of water vapour*—as opening up a new field in science, and in a second article (Oddo, *Gazz. chim. ital.*, [1] 1915, xlv., 395) remarkable deductions were drawn therefrom upon such diverse topics as atmospheric electricity, the influence of temperature on vegetation, the respiratory processes of plants and animals, the electrolytic reactions in a monocellular organism, and

*Presented at the Buffalo Meeting of the American Chemical Society, April 10, 1919.

the first experimental mechanism for the origin of life.

An adequate discussion of so many important questions cannot be entered into here, but since the molecular weight of water vapour is a matter of fundamental interest in a few minor fields (such as the modern theory of solutions and steam engineering practice) it has been thought profitable to subject the mutually contradictory conclusions of Bose and Oddo to a critical examination, particularly since these conclusions are now quoted without reserve in standard monographs (Turner "Molecular Association," 1915, p. 89). The results below 32° may first be considered.

According to Oddo, saturated water vapour below 32° is partly dissociated into hydrogen and hydroxyl ions. At 0° the calculated degree of ionisation is 2·6 per cent, the vapour pressure being 4·6 mm. From these figures we can determine the concentration of hydrogen and hydroxyl ions in saturated vapour at 0°. The value obtained is $7 \times 10^{-6}$ g. ions per litre, in other words, just 200 times as great as the corresponding concentration in pure liquid water at 0° (Kohlrausch and Heydweiller, *Z. physik. Chem.*, 1894, xiv., 317). Since the mobility of the ions in the vapour phase would certainly be enormously greater than in the liquid, owing to the diminished viscosity of the medium, it follows that the conductivity of saturated water vapour (or air saturated with water vapour) at 0° should be comparable with that of a fairly concentrated salt solution. Now this is admittedly not the case, hence Oddo's whole argument must be quite invalid.

The explanation is not far to seek. Regnault's data at temperatures below the normal (although smoothed off on a curve to render them consistent) are far too inaccurate to be employed as a basis for determinations of molecular weights to the second place of decimals. In fact, the density of the saturated vapour at pressures so low as 4·6 mm. becomes so small that it is impossible to measure it with anything approaching the above order of accuracy. Even the exceedingly careful determinations of Young (Young, *Proc. Roy. Soc.* Dublin, 1910, xii., 374) on the specific volumes of the saturated vapour of 30 organic liquids are conceded to be uncertain at the lower temperatures investigated, for this same reason. Consequently, until more definite proof of this spontaneous ionisation of water vapour is brought forward, we cannot consider the molecular weight of water vapour to be appreciably diverted from the normal value as a consequence of such ionisation. (The dielectric constant of water vapour is so near to unity as to appear to preclude more than the merest trace of ionisation--Bädeker, *Z. physik. Chem.*, 1901, xxxvi., 305).

It remains to examine the abnormally high vapour densities for temperatures above normal, upon which both Bose and Oddo postulate the equilibrium $(H_2O)_2 \rightleftarrows 2H_2O$. Bose's calculations are dependent entirely upon a series of 19 determinations at 13 different temperatures ($T$ ranging from 50° to 182°, $p$ ranging from 52·6 to 790 mm.) by Kornatz. It is true that a few isolated measurements of previous investigators are quoted, which are in fair agreement with these results, but of the many determinations which do not agree no mention is made.

While Kornatz's measurements certainly indicate a greater vapour density than the theoretical for monomolecular water throughout the whole series, yet examination shows that *at any one temperature* the observed variation in density with pressure is *systematically* different from that calculated by the use of Bose's equation for the equilibrium: $(H_2O)_2 \rightleftarrows 2H_2O$. The following table will illustrate this clearly. Densities are given relative to air; the theoretical ratio for monomolecular water is 0·6216.

| $T$ (abs.) | $p$ (mm. Hg) | Density (obs.) | Variation with $p$. | Density (calc.). | Variation with $p$. |
|---|---|---|---|---|---|
| 348 | 86·8 | 0·6324 | 0·0095 | 0·6307 | 0·0139 |
| 348 | 231·5 | 0·6419 | | 0·6446 | |
| 353 | 71·0 | 0·6308 | 0·0063 | 0·6276 | 0·0144 |
| 353 | 249·0 | 0·6371 | | 0·6420 | |
| 358 | 86·76 | 0·6307 | 0·0052 | 0·6278 | 0·0116 |
| 358 | 260·3 | 0·6359 | | 0·6394 | |
| 363 | 52·6 | 0·6286 | 0·0061 | 0·6247 | 0·0119 |
| 363 | 263·0 | 0·6347 | | 0·6366 | |
| 368 | 63·4 | 0·6282 | 0·0051 | 0·6247 | 0·0091 |
| 368 | 253·6 | 0·6333 | | 0·6338 | |

It will be evident from the above table that the observed variation is approximately only 50 per cent of the calculated. Bose remarks, in a passing comment on this fact, that it is possible that the experimental results are affected by systematic errors, which may be partially explained by assuming that the equilibrium $(H_2O)_2 \rightleftarrows 2H_2O$ in the vapour phase is only slowly established. It is extremely improbable that this assumption is correct, since even in liquid water no indication of anything but instantaneous equilibria between the different molecular species present has ever been obtained. If Kornatz's data *are* trustworthy, Bose's interpretation of them is not justified; if they are *not* trustworthy, no such interpretation should have been attempted.

We are consequently left to face the fact that, while vapour density measurements for temperatures above the ordinary give abnormally high results, these high results cannot be adequately explained by assuming association in the vapour phase. Indeed, other evidence renders it certain that such association is negligible even at 100°. Let us compare the abnormality in the density of saturated water vapour at this temperature with the abnormalities shown by the saturated vapours of other liquids at their boiling points. The data in the following table are taken from Washburn (Washburn, "Principles of Physical Chemistry," 1915, p. 31).

| Liquid | Boiling point °C | Vapour density (observed / calculated) | Vapour density (observed / corrected) |
|---|---|---|---|
| Benzene | 80·1 | 1·024 | 0·990 |
| Pentane | 36·3 | 1·046 | 1·002 |
| Heptane | 98·4 | 1·055 | 1·007 |
| Chlorobenzene | 132·0 | 1·055 | 1·019 |
| Nitrogen | —195·7 | 1·05 | 1·00 |
| Helium | —268·5 | 1·09 | — |
| Water | 100·0 | 1·028* | 1·018† |

* Value taken from Regnault's determinations· see Oddo, *Gazz. chim. ital.*, [1], 1915, xlv., 328.

† Critical data employed were taken from Holborn and Baumann, *Ann. Physik.*, [4] 1910. xxxi., 945.

The ratios obtained in the third column show that all substances (even such generally accepted non-associated liquids as the saturated hydrocarbons and the inert gases) give saturated vapours of abnormally high density even at pressures as low as one atmosphere. As has been pointed out by Guye (Guye, *Trans. Faraday Soc.*, 1910, vi., 84), the assumption of the merest trace of association in the vapour phase involves extreme association in the more concentrated liquid phase, consequently if the above abnormalities are due to molecular complexity in the vapour state than even the so-called "normal" liquids are all exceedingly complex. While it would be going too far to state that we have *no* indications of association in the liquid state for the substances listed above, yet their general physical properties show conclusively that any deviations from ideality are very slight (Dolezalek has recently claimed (*Z. physik. Chem.*, 1919, xciii., 585), that liquid argon is slightly associated, but rightly notes that such association does not extend appreciably unto the vapour phase).

To what, then, are the abnormalities due? To the simple fact that the saturated vapours under discussion do not exactly follow the gas laws, but require a correction according to the equation of state. When such a correction is applied (as has been done in the last column of the above table by means of Berthelot's modification of van der Waal's equation) the abnormalities practically disappear (see Washburn, *loc. cit.*, p. 33).

It will be noticed that water vapour diverges *less* than the "theoretical" than the majority of substances listed. Have we any more reason to attribute the abnormalities here to the presence of dimolecular $(H_2O)_2$ than we have to postulate polymerisation in pentane vapour or the existence of $He_2$ in helium gas? It is true that liquid water is highly associated, and that the vapours of certain similarly associated liquids such as acetic acid (Young, *loc. cit.*) show unmistakable association even at low temperatures, yet from the values obtained in the table above it is evident that, below 100° at least, association in water vapour can only be minute. While the observed vapour density is still slightly above the corrected theoretical value, yet the excess is not so great as in the case of chlorobendene and may be accounted for in part by uncertainty in the critical data. (If association exists at the critical point, the crtical data are not strictly applicable to the Berhelot equation). At temperatures approaching the critical, where the pressure is very high, association of the saturated vapour may become appreciable, but the extensive association claimed by Bose and Oddo at temperatures below the boiling point is certainly an exaggeration of the facts. (The experiments of Ramsay and Young (*Phil. Trans.*, 1892, clxxxiii., 107), indicate a rapid increase in the ratio (obs./calc.) above 200°. At 270° the observed vapour density is more than 15 per cent. in excess of the corrected theoretical).

In conclusion, it is necessary to record a protest against the optimistic habits prevalent among writers of text books as well as of original articles, of treating all gases as perfect. In work on gaseous systems, it is rare to find any correction applied for "the equation of state," although frequently intricate calculations which pre-suppose considerable accuracy are carried out with the use of the observed densities. In techncal processes (probably following Haber's "Thermodynamics of Technical Gas Reactions" and similar monographs) no regard at all is commonly paid to possible abnormalities, even when reactions under high pressures are considered. That the quantities of different gases introduced into the reaction vessels under such conditions are quite at variance from the correct proportions has been strikingly shown in recent work on the Haber process ("Physical and Chemical Data of Nitrogen Compounds," 1918, p. 5-6 (M.I.D. Research Laboratory, University College, London)). The extended discussion of this general question given by Lewis in several articles does not appear to have attracted the attention which it deserves (G. N. Lewis, *Proc. Am. Acad.*, 1901, xxxvii., 66, etc.; 1907, xliii., 262; *Journ. Am. Chem. Soc.*, 1915, xxxvii., 2309).

For the same reason, vapour density determinations upon dissociating substances, such as phosphorus pentachloride and the ammonium halides (Smith and Lombard, *Journ. Am. Chem. Soc.*, 1915, xxxvii., 38, 2055), will not furnish exact values for their dissociation unless correction is made for the appreciable divergence from the perfect gas laws of all of the substances concerned in the equilibrium. The possible error in functions derived from *variations* in the calculated degrees of dissociation (such as the heat of dissociation) will naturally be much greater (Smith and Lombard, *loc. cit.*, p. 55). To attempt to obtain quantitative values for the association of *liquid* water from uncorrected vapor density measurements, as has been done by Guye is obviously altogether futile (Guye, *Trans. Faraday Soc.*, 1910, vi., 84).

In the standard Victor Meyer vapour-density experiment the text-books on practical physical chemistry "allow" the student an error of "less than 5 per cent," although the abnormalities in the vapour densities of many common liquids exceed that value. Since corrections of less than 1 per cent (*e.g.*, for the water vapour content of the atmosphere) have been proposed (Evans, *Journ. Am. Chem. Soc.*, 1913, xxxv., 958), it would evidently be well worth while to introduce the equation of state factor into the discussion. Otherwise, the accurate student and the conscientous instructor will inevitably clash, without prospect of reconciliation.

*Summary.*

The monomolecular nature of water vapour has recently been questioned, "spontaneous ionisation" of $H_2O$ into $H^+$ and $OH^-$ at low temperatures and association into $(H_2O)_2$ at higher temperatures being postulated. It has been shown here that the evidence for the existence of the equilibria

$$H_2O \rightleftarrows H^+ + OH^- \text{ and } 2H_2O \rightleftarrows (H_2O)_2$$

is in each case entirely insufficient, that the abnormalities in the vapour densities of normal substances at their boiling points are similar to that in water vapour at 100°, and that such abnormalities practically vanish on applying the corrections for deviation from the perfect gas laws.

An "equation of state" correction is similarly necessary in gas reactions at high pressures, in calculations on dissociation in the vapour state and in Dumas or Victor Meyer vapour-density determinations.—*Journal of the American Chemical Society*, December, 1920.

## THE DEVELOPMENT OF THE CHEMICAL INDUSTRY IN THE FORMER PRUSSIAN POLAND.

The chemical industry in that part of Poland which was known before the war as Prussian Poland gives signs of a sound and remarkable development. Its productivity has been recently extended in the field of the chemical by-products of alcohol. The distilleries of Posen and Pomerania have been united in a big concern "Akwawit Rectification of Alcohol and Chemical Factory." The head office of this new Company is in Poznan (Posen).

Considering the natural wealth of this province of Poland as regards alcohol, high hopes are entertained that the exports of its by-products will contribute considerably to the improvement of the economic position of the country in the international market.

The Company has acquired all the distilleries situated in Poland, belonging to the firms C. A F. Kahlbaum of Berlin, and Breslauer Distillery of the Charlottenburg Company. The subscribed capital of the "Akwawit" Company amounts to 20,000,000 marks. The chief subscribers are The Land Bank of Posen (2,500,000 marks), The Kwilecki Potocki & Co. Bank (2,500,000 marks), The Co-operatives Union Bank (1,000,000 marks), The Commercial Bank of Posen (11,700,000 marks), C. A. F. Kahlbaum (2,000,000 marks).

The Board of Control consists of 18 members; among them there are eight landowners and five bank directors.

A few more facts pointing to the development of the chemical industry deserve some attention.

A new chemical factory has been founded in Glowno near Posen; it is called "Posen Chemical Works of K. Chmielewski." Another big concern founded in May, 1920, known as the "Luban Potato By-Products Factory" has published a report which shows that up to September 30, 1920, its net profits amounted to 3,719,423 marks. This Company has already acquired the starch factory in Torun (Thorn) which belonged to the German concern known as "Deutsche Bruder Unitat in Herrnhut," and it proposes to buy out other German factories, situated in Polish territory, especially the branches of the famous German firm C. A. Kohlman & Co., of Frankfurt-an-Oder. The Luban branch of this firm is already run by the Polish "Luban Potato By-Products Factory" which has acquired the rights of tenancy.

These Luban factories producing potato meal, starch, dextrine, soluble starch, and potato pulp, constitute the biggest concern of this kind in Poland, and are capable of working daily 20 to 22 wagons of potatoes. Owing to the requisition of potatoes by the Food Ministry, the factories have been compelled to work only at short time. The greater part of the produced potato meal has been exported to France, England, and Germany, the rest has been used for home consumption. The lack of transport has made the exports very difficult. The exports for France have been transported by trains supplied by the French Mission.

The production of dextrine was possible, only on a small scale; it has been consumed chiefly by the textile industry in Lodz and Bielsk.

Owing to the devaluation of Polish money, high prices of raw materials, and rising costs of transport, the company proposes to raise its capital to 20,000,000 marks.

Similarly, the wholesale druggist factory in Posen has increased its capital to 15,000,000 marks.

The Pharmaceutical Products Factory "Bareikowski & Co." shows a net profit for the year 1919-1920 of 987,000 marks. Out of this amount 400,000 marks have been given away for social purposes. This factory has increased considerably its activity through opening branches in Gdansk (Danzig) and Warsaw. Its capital has been raised to 15,000,000 marks.

A factory of matches ("Zygaunt Stabrowski") has been started in Posen; a company has been formed in Bydgoszcs (Bromberg) with the view of starting another factory of matches, the subscribed capital amounts already to 3,000,000 marks.

The relation between imports and exports may be shown as follows:—

For the period of July 1, 1919 to January 1, 1920, the imports of chemical products into Poland amounted to 9,000,000 marks, and for the period from January 1, 1920 to October 1, 1920 to 87,000,000 marks. The exports from Poland for the period from September 1, 1920 to January 1, 1920 amounted to 3,000,000 marks, and from January 1, 1920 to October 1, 1920 only to 609,000 marks.

## COLOUR TEST FOR OXALIC ACID.

By LEWIS H. CHEINOFF Denver, Colo.

A few crystals of resorcinol are added to about 5 cc. of the unknown solution in a test tube, and the mixture is warmed slightly to dissolve the resorcinol. It is then cooled and 5 cc. of concentrated sulphuric acid is carefully and slowly poured in along the side of the tube so as to form a layer. A blue ring will be formed at the juncture of the two layers, if oxalic acid is present. The colour is best seen if held to the light in front of a sheet of white paper. Care must be taken that the mixture does not warm up appreciably. If the blue colour does not appear in a few minutes, the mixture is shaken thoroughly, and, after cooling somewhat, 5 cc. more of sulphuric acid is added. Should the colour still fail to appear, the mixed contents of the tube should be gently warmed over a flame (not boiled) when an indigo blue colour will diffuse throughout the liquid. If the mixture be cooled with ice-water, the colour will disappear only to reappear again on heating. If the mixture be boiled a few minutes, the colour will turn a deep dark *green*, which will become a light yellow-green on cooling. If to the cold yellow-green solution an equal volume of sulphuric acid be added so as to form two layers, the *blue* colour will again appear. It is believed that all these reactions taken together are characteristic of oxalic acid alone.

This test may be made sensitive to one milligrm. if the dry unknown substance be warmed with two drops of a 10 per cent aqueous resorcinol solution and the sulphuric acid added drop by drop. The blue colour then appears immediately. For very

dilute solutions of oxalic acid or its salts, it is best to evaporate to a concentration of about 10 per cent.

If interfering substances are present the oxalic acid may be precipitated in ammoniacal solution as the calcium salt, washed with water, and the test applied directly to an aqueous suspension of the salt.—*Journ. Am. Chem. Soc.*, Sept.

## CORRESPONDENCE.

### COLOUR OF WATER.

*To the Editor of the Chemical News.*

SIR,—With reference to my note on the above subject in your Journal of Jan. 7, 1921 (cxxii., p. 9), the second "Sir" in the first line should be deleted.

Bancroft also discussed (CHEMICAL NEWS, 1919, cxviii.) the question as to whether the colour of water is due to the scattering of light by suspended particles. This subject has been studied recently by W. H. Martin (*Journ. Phys. Chem.*, 1920, xxiv., 478). He prepared dust-free water by distillation in vacuo, by precipitating gelatinous zinc, cadmium, and aluminium hydroxides from solution of the sulphates, and by cataphoresis of water (see *inter alia*, T. R. Briggs, "Second Rep. on Colloid Chem.," B.A., 1918, pp. 26-52; and also Ormandy, Somerville, and Northall-Laurie; CHEMICAL NEWS, 1920, cxxi., p. 14; and Ormandy, *ibid.*, p. 301).

Martin found that all the dust-free liquids which he examined scattered light, that of short wave length more than of long wave length. The intensity of the scattered light from dust-free water was found to be 0·06 (toluene=1), a comparatively low value, that for, *e.g.*, $\alpha$-chloronapthalene being 4·3. Martin also found that the scattered light is very largely plane polarised from liquids which scatter little light (*i.e.*, water) and the polarisation in different liquids decreases as the relative intensity of the scattered light increases, and he showed that phenomena which he observed are really ducto light-scattering and not to fluorescence (for recent work on this subject in connection with the gases H, N, air, O, $CO_2$, and $N_2O$ (see Rayleigh, *Proc. Roy. Soc.*, 1920, xcvii., 485; CHEMICAL NEWS, 1920, cxxi., 42), and for He and Ar (Rayleigh, *Proc. Roy. Soc.*, 1920, xcviii., 57)).

Regarding the work of Ducleaux and Wollemann (see CHEMICAL NEWS, 1921, cxxii., 9) it is instructive to note that Ramsay and Shields (*Zeitschr. physikal Chem.*, 1893, xii., 464; *Journ. Chem. Soc.*, 1893, lxiii., 1089) from measurements of surface tension, found that the formula of water at 0° is $(H_2O)_4$. This to some extent confirms the hypothesis of Ducleaux and Wollemann, inasmuch as the formula of water is shown to be $(H_2O)_4$ at 0°, and a mixture of $H_2O.(H_2O)_2$ molecules at 100° (from vapour density of steam).—I am, &c.,

E. TOMKINSON.

**Walney, Barrow-in-Furness, 8th January, 1921.**

## NOTES.

BRITISH INDUSTRIES FAIR.—The arrangements are well in hand for the forthcoming British Industries Fair to be held at London (organised by the Department of Overseas Trade), and Glasgow and Birmingham. The London and Birmingham Fairs run concurrently from February 21 to March 4, while the Glasgow Exhibition opens a week later on February 28. Intending visitors will therefore have no difficulty in getting from one section to another. Only British manufacturing firms are allowed to show and the goods must be of the exhibitor's actual manufacture. The Glasgow Exhibition will have considerable interest for the chemical manufacturing trades, inasmuch as its schedule includes chemicals (heavy and light), domestic chemical products and dyes, while at London, places are given to drugs and druggists' sundries, photographic apparatus, scientific and optical instruments, and glassware of all descriptions. Manufactured metal goods, general hardware, guns, small tools, weighing instruments, and motorcycles and cycles will be important features at the Birmingham Fair, and a position of prominence is given to paints, colours, oils and varnishes and painters' requisites, and to nautical scientific instruments and apparatus. Lighting and heating appliances form a much larger section than last year.

BOARD OF TRADE ANNOUNCEMENT.—In pursuance of the powers conferred upon them by Section 4 (1) of the Gas Regulation Act, 1920, the Board of Trade have appointed Sir R. T. Glazebrook, K.C.B., F.R.S., to be Chief Gas Examiner under that Act, and Mr. C. V. Boys, F.R.S., Mr. J. S. Haldane, F.R.S., and Mr. W. J. Atkinson Butterfield, M.A., F.I.C., F.C.S., to be Gas Referees. The Board have also appointed Mr. H. C. Honey to be Director of Gas Administration in the Power Transport and Economic Department, Board of Trade Offices, Great George Street, S.W.1. Furthermore, in pursuance of the provisions of Section 2 (4) of the above-mentioned Act, the Board have appointed Sir William Pearce, M.P. (Chairman), Dr. T. Carnwath, D.S.O., M.B., Mr. William Doig Gibb, O.B.E., M.Inst.C.E., and Dr. T. Gray, D.Sc., Ph.D., to be a Committee to enquire whether it is necessary or desirable to prescribe any limitation of the proportion of carbon-monoxide which may be supplied in gas used for domestic purposes, and also Mr James Hunter Gray, K.C. (Chairman), Mr. W. J. Atkinson Butterfield, M.A., F.I.C., F.C.S., and Dr. C. H. Lander, D.Sc., M.I.M.E., A.M.I.C.E., to enquire whether it is necessary or desirable to prescribe any limitations of the proportions of incombustible constituents which may be supplied in gas. Communications may be addressed to the Secretary to each of these Committees at the Power Transport and Economic Department, Board of Trade, Great George Street, S.W.1.

HYDROGEN PEROXIDE AND FLOUR.—The method employed to analyse catalase in milk by measurement of the volume of oxygen disengaged in contact with a certain quantity of hydrogen peroxide is applied by M. Marion to wheat flour. Thus the degree of purity can be determined and also that of milling.—*Comptes Rendus*, October 26. 1920.

CYANAMIDE AND DICYANAMIDE IN CALCIC CYANAMIDE.—The most frequent analyses of calcic cyanamide relate to (1) total nitrogen; (2) nitrogen of cyanamide; (3) nitrogen of the dicyanamid. Analysis of the total nitrogen is made by the Kjeldahl method. As for the cyanamide and dicyanamide nitrogen, analyses are based upon the following reaction. (1) Solution of calcic cyanogen gives with nitrate of silver and in presence of ammonia an argentic precipitate containing all the nitrogen of the cyanamide. (2) An aqueous solution of dicyanamide does not precipitate with nitrate of silver in presence of $NH_3$, but gives a precipitate when the ammoniacal solution is boiled with excess of NaOH or KOH. Thus an argentic precipitate of dicyanamide can be obtained with the ammoniacal mother liquor from precipitation of the cyanamide. Some authors (Kappen for cyanamide, and Ulpiani, dicyanamide) proposed an estimate of the silver in the argentic precipitates, with $AgNO_3$ and $CNSNH_4$. Confirming what had already been noted by Caro with argentic cyanamide, Messrs. Marqueyrol, Loriette and Desvergnes, noted that the silver in the argentic precipitates was in variable proportion for cyanamide and that the argentic dicyanamide was particularly soluble in water. The only method which gives precise results is quantitative analysis of the nitrogen in the argentic precipitates, estimating from this analysis the percentage of cyanamide and dicyanamide.—*Bull. Soc. Chim. de France*, November 20 1920.

LINSEED OIL SUBSTITUTES.—The last number of *Revue de Chimie Industrielle* draws attention to an error they made in setting up the type, lines of one paragraph being mixed with another It should read as follows from line ending "linseed oils":—"If one wishes to give siccative properties to non-siccatives such as fish oils it suffices to add varnish to them. The fish oil is first boiled in presence of the necessary metallic siccatives, then the hot linseed oil is poured slowly into it so that there will not be a fall of temperature. When fish oil is subjected to the action of ozonised gas in presence of spongy platinum they acquire siccative properties A product is obtained similar to the lacquer of Rapolin by boiling thick oils (20 kilogrms. linseed oil and wood oil) with 10 of Brazil copal at about 280° C. The temperature is let fall to 160° C. and 50 grms. of flowers of sulphur added, 40 grms. paraffin; 110 grms. rubber solution; 60 grms. mirbane essence; 6 kilogrms. spirit of turpentine, and 6 of benzine." The last 18 lines belonged to another paragraph.

## New Patents.

THIS List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W.C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

36581—Anderson, J.—Fusion of organic substances with alkalies. Dec. 30th
36536—British Dyestuffs Corporation—Manufacture of oxy and sulpho-oxy derivatives of anthraquinone. Dec. 30th.
36377—Chemische Fabrik Flora.—Manufacture of silver thioglycolate of sodium. Dec. 29th.
36712—Cook, D—Chemical and physical synthesic. Dec 31st.
36476—Fitzgerald F. W. V.—Preparation of substitutes for vulcanite horn, etc from blood Dec. 30th.
36644—Moulin, R.—Apparatus for diffusion of essence or volatile liquids Dec 31st.
36465—Plauson, H.—Manufacture of phosphatic manures. Dec. 30th.
36558—Plauson, H.—Oxidation of acetaldehyde to acetic acid. Dec. 31st.
36286—Watson J.—Method of treating mineral stained barytes to produce a pure white. Dec. 29th.
757—Aschkenasi, L.—Manufacture of perborates and di-sodium-phosphates Jan. 7th
471—Blanc, G A—Extraction of Potash from leucite or leucite rocks. Jan. 5th
121—Bleicen, B—Apparatus for production of distilled water. Jan 3rd
515—Boocock, M.—Recovery of ammonia from ammoniacal-liquor. Jan. 6th.
414—Burke O'Donogon.—Manufacture of lithopone zinc sulphide and ammonia. Jan 5th.
519—Deutsche Gold-und Silber-Scheideanstalt vorm Rossler—Manufacture of acetone. Jan. 6th.
885—Norsk Hydro-Elektrisk Kvalstofaktieselskab—Apparatus for effecting continuous crystallization of solutions Jan. 7th.

*Specifications Published this Week.*

155600—Head, C. J.—Method for the production of metallic tungsten power direct from sodium and potrasium tungstates.
155609—Sauer, J N. A—Process for the purification and separation or filtiation of liquids or liquors.
136061—Jaloustre, L. A. and Knifetz, Z. and Warchabsky, M.—Process for the production of condensation products of phenois and aldehydes.
155692—Hood, J. J.—Purification of Sulphur.
141059—Mrreau C. and Dufraisse, C—Condensation products of acrolein with phenols.
126625—Desachy, P.—Process for the manufacture of anhydrous zinc sulphide.
137071—Norsk Hydro-Elektrisk Kvelstofaktieselskab.—Production of concentrated nitrous gases and nitric acid.
145732—Krupp Akt.—Ges. F.—Acid-resisting receptacles such as boilers, pipes and the like.

*Abstract Published this Week.*

*Zirconium Salts*—Mr. H. Wade, of Hatton Garden has obtained a Patent No. 153113 for a new basic sulphate of Zirconium of the composition $5ZrO_2$, $3SO_3$, $13H_2O$ free from iron titanium, and silicon is obtained by adding sulphuric acid in the requisite quantity to a solution of zirconium oxychloride containing free acid preferably hydrochloride acid. The basic sulphate is precipitated on heating.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and forward on post free for the official price of 1/- each.

## MEETINGS FOR THE WEEK.

*Monday, January 24, 1921.*

Royal Society of Arts, 8. "Aero Engines," by A. E. L Chorlton.

*Tuesday, January 25.*

Royal Institution, 3. "The Progress of Geodesy in India," by Sir Gerald P. Lenox-Conyngham.
Institution of Electrical Engineers, 7. (At Leeds).

*Wednesday, January 26.*

Royal Society of Arts, 4.30. "Origin and Development of the Research Associations established by the Department of Scientific and Industrial Research," by A. Abbott.
Society of Chemical Industry, 7. (At Nottingham).

*Thursday, January 27.*

Royal Institution, 3. "Biochemistry (Vitamins)," by Dr. Arthur Harden.
Institution of Electrical Engineers, 6. "Temperature Limits of Large Alternators," by G. A. Juhlin.

*Friday, January 28.*

Royal Institution, 9. "Cloudland Studies," by Sir James Dewar.
Physical Society, 5.
Institute of Metals, 7.30. (At Sheffield).

*Saturday, January 29.*

Royal Institution, 3. "The Madrigal (Key)," by Dr. P. C. Buck.

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## CONSTITUTION OF MATTER AND ELECTRICITY*

By A N. SRIVASTRA.

IN this article the author hesitatingly attempts to express certain ideas regarding the structure of the atom and the constitution of matter and electricity, which, though in direct contradiction to the existing notions on the subject, might be of interest to some speculative minds. In this system of chemical philosophy, aether is believed to be the matter of matter and in it,

'Wrapt in mystic silence and gloom"
The slumbering secrets of creation lie."

Matter is aether condensed, and electricity is aether in motion. The electron at rest has no meaning, and it is motion that justifies its existence. The central nucleus is aether condensed, and thus excessively fine grained, capable of throwing out small particles, like the planets once shot from the sun. The electrons in the orbit are responsible for all the physical and chemical properties of the atom, and the phenomenon of radio-activity involves a derangement, both in the system of electrons and the central nucleus itself. The relative positions of the electrons, the diameter of their orbits, and their velocities, are determined by the charge of the nucleus and the field of force to which this charge gives rise. The number of electrons in motion round the positively charged nucleus in an atom is of the order of the half the atomic weight for the lighter elements. For an accurate determination of these numbers we are indebted to Mr. H. G. J. Moseley, but the evidence of his experiments is only comparative, not absolute. Thus, if the atomic number for hydrogen be $n$, for helium it is $n+1$, for lithium $n+2$, and so on. Moseley fixed the atomic number for hydrogen as 1, and then He is 2, Li 3, and so forth.

In the meantime, the existence of two light gases, coronium and nebulium, between hydrogen and helium, has been suggested by Rydberg. Prof. Rydberg, therefore, proposes that the atomic numbers be converted into ordinals by adding two units to all the elements but hydrogen. This would not, although, affect Moseley's data, but measurements of the scattering of X-rays by gases indicate consecutive numbers for hydrogen and helium. This difficulty can be overcome by placing the two hypothetical elements before hydrogen instead of after. This was the notion held by Mendeleeff. Coronium is his element, with an atomic weight $\frac{1}{2}$, existing in the corona of the sun, and nebulium is his element. The aether, with an atomic structure and an insignificantly small atomic weight. As there seems to be no near possibility of other elements of low atomic weight, we may place aether as the element with zero atomic number (compare with Rydberg's electron gas). Coronium, on this table, will have an atomic number 1, and Moseley's numbers have to be increased by one unit.

Next turn to the question, the structure of the nucleus as understood by modern scientists. In connection, reference may be made to an article by Prof. A. Berthond, that appeared in the April numbers of the CHEMICAL NEWS. Prof. Berthond states, "the positive charge of the nucleus does not represent merely the number of positive electrons which the nucleus contains. There is no doubt that the negative electrons also enter into its constitution. The apparent charge is determined by the number of positive electrons in excess as compared with the negative electrons. It is, however, probable that with hydrogen the atomic nucleus reduces to a single positve electron, the mass of which is 1830 times that of the negative electron." And further, "thus the positive electron reveals itself as the smallest corpuscle which enters into the constitution of matter, and at the same time as that to which bodies owe almost the whole of their weight." The positive electron is assumed to be the basis of all matter. Why then is the negative electron 1830 times lighter? It is a corpuscle of electricity, but with the thought as to the nature of electricity the professor is lost in the wilderness It has been loosely said, "Matter is an aggregate of positive and negative electricity." Still, the very fact that positive and negative electricity destroy each other renders such an idea inconceivable. Positive electricity is not the absence of negative electricity. The two are related like the positive and negative quantities in algebra. Thus, in our conception, as the negative electricity is produced by the motion of indefinitely small aether particles round the nucleus, at a tremendous in an anti-clockwise direction, the nucleus rotating round its axis in a clockwise direction generates positive electricity, and the two annul each other.

To our imagination the nucleus, therefore, appears as an aggregation of highly-condensed aether particles, which for some unknown reasons group themselves into hydrogen or helium nuclei on detachment from the parent nucleus. Another extract will illustrate the hopeless confusion and self-contradiction arising out of a belief in the positive electrons. Here is another quotation from Prof. Berthond: "Thus an electron appears as a corpuscle of electricity, devoid of any basis of matter; in the ordinary sense of the word it is at one and the same time the elementary particle of negative electricity, and an elementary particle of matter." In fact, it is a mistaken notion in science to identify electricity with matter. Matter and energy manifest in motion are two entirely different things, although both of them convey the idea of mass.

As a last point, it may be emphasised that the electrons which take part in a radio-active change seem to be those in the outer rings, as the transformation of an element is always accompanied by a change of valency, and the shifting of an electron from one ring to another liberates vast quantities of energy.

The idea enunciated in these columns gains additional strength on account of its similarity to known astronomical phenomena. Thus we may fancy the electron revolving round the nucleus, much in the same way as the earth does round the sun, and so forth. This is all but a hopeful speculation, and as such I commend it to our readers.

* Extract from a paper read before The Students' Society, Lucknow by the kind permission of Mr. M. P. Nigam, B.Sc., Secretary.

## NOTES ON THE HIGH-LEVEL DIAMOND DEPOSITS OF BRAZIL.

By A. M. PONTIE, A Inst M M.

DIAMONDS were first discovered in Brazil in 1729, at a place called Tijuca, in the State of Minas Geraes.

They are found in two distinct varieties of deposits:

1. In recent gravels, or ancient river terraces
2. In high-level areas, which by many are thought to be conglomerates of fluviatile origin.

Many of the rivers of Brazil, though situated far apart, carry diamonds in greater or less quantities, the principal of these being.

The Jequitinhonha, near the town of Diamantina, Bagagem, Somno, Sao Antonio, Prata, Abaeté, Sao Francisco, in Minas, Paraguassú, in the State of Bahia, Tibaji, in Paraná, and many streams in Matto Grosso and Goyaz.

High-level diamond bearing deposits exist in many of the upper basins of these rivers; the best known are, Sao Joao da Chapada, Dattas, Serrinha and Bôa Vista, near Diamantina, Grao Mogol, about 120 miles further north, Agua Suja, near the town of Bagagem, and Lençoes, District of Bahia.

The majority of these high-level deposits are situated on the dividing ridges of the streams, several hundred feet above the present river valleys.

The discovery of diamonds in the high-level deposits dates from 1834, when an old slave woman found a large stone embedded in blue clay; this led others to investigate the formation, with the result that the locality, Sao Joao da Chapada has been worked for many years with very satisfactory returns.

For a number of years before this discovery, no attempt had been made to ascertain the source whence the diamond-bearing gravels of the rivers and valleys had acquired their precious stones. The great richness of these gravels, and the cheap slave labour, probably satisfied the then owners, and no doubt, lack of initiative and curiosity deterred them from studying the problem more fully. Prospecting in a country like Brazil is not at all easy; the lack of roads, the dense forests and thick undergrowth handicap the traveller, and the country is mostly covered with a thick coating of surface soil which obscures the underlying rock formation. Moreover, the insect pests which abound make the life of the explorer a perfect misery.

The most important high-level deposits so far located, are situated in the Serra do Espinhaço. This range of mountains extends northward from Ouro Preto to Joazeiro, a distance of about 620 miles, with a width of nearly 40 miles in its widest section. Some of the rivers rising from the higher eminences of this Serra have yielded the bulk of the diamonds.

The Serra do Espinhaço is flanked on the west by the valley of the Rio Sao Francisco, and on the east by the granitic and schistose foot hills, which extend to the Atlantic; the general altitude of the Serra is about 1500ft. above sea level, though many of the peaks rise to 4600ft.

*A Paper discussed at the Meeting of the Institution of Mining and Metallurgy, on Thursday, January, 20th, 1921.

The Serra is composed of a series of rocks, consisting of alterations of quartzites, with yellow and grey shales. These different beds occur throughout the series. The general dip of the strata is to the west towards the valley of the Sao Francisco, though it frequently alters and a reverse dip occurs. Where unweathered, the quartzites consist of a hard mass, made up of minute rounded grains of quartz, but where affected by considerable weathering, the quartzite is altered into soft sand-stone. The quartzites and sandstones are stratified and false bedded, the interbedded shales are laminated and generally slaty in structure. Quartz veins are abundant in both the quartzites and shales. Gold occurs in many of these veins There are also thin layers of quartz conglomerates interbedded in the quartzites. The Espinhaço quartzite near the town of Diamantina, where extensive weathering has taken place, shows many lines of faulting, slightly inclined beds butting up against vertical or over turned strata These phenomena are evidence of the enormous amount of pressure which must, at one time, have taken place.

The most important, though perhaps the least known, high-level diamond bearing deposits of the Serra do Espinhaço, are Serrinha, Bôa Vista, and Sao Joao do Barra.

The *Serrinha* deposit is situated eight miles south-east from the town of Diamantina.

This deposit lies on the crest of a mound, situated at the foot of a vertical cliff formed at this point by the uplifting of the Serra do Espinhaço.

The diamond-bearing ground covers an area of about half a square mile. Owing to lack of water on the ground and the altitude of the deposit, about 1000ft. above the river which flows at its base, regular and continuous work is not being carried out. The ground is well exposed by the existing cuttings and pits, in many places to a depth of over 40ft. On careful examination of the walls of these cuttings, it is evident that this deposit is a breccia consisting of boulders of soft sandstone, seldom more than a foot, or less than 3in. in diameter, angular in shape, with blunted corners. These boulders, some of which are flat and stand on edge, are embedded in a blue-grey mass, which contains a few rounded pebbles of quartz no doubt derived from the conglomerate beds in the Espinhaço quartzites. The boulders rarely touch one another, and are completely surrounded by the cementing mineral, which shows lines of schistose material curving round them. Small veins of iron oxide running through the mass are not uncommon.

The breccia has the characteristic of being able to stand in a vertical position. Clear faces 200 to 300ft. in length by 40ft. in depth, are exposed to view The whole mass of mineral is soft, and readily disintegrates under the influence of a stream of water from a hydraulic nozzle, with 50lb. pressure per square inch.

Concentrates by jigging show the following minerals:

Magaetitie, small octahedra, abundant, sp. gr. 5·0.
Hematite, abundant, sp. gr. 4·5 to 5 3.
Martite, abundant, sp. gr. 5·2.
Pyrope garnets, rare sp. gr.
Some tourmaline and mica, rare, sp. gr. about 3·5.
Diamonds.

The diamonds are white and of very high quality, faulty stones being comparatively rare, under 2 per cent of the whole number. The small stones are valued locally at per carat, 4 and 5 carat stones are frequent, and there are very few under one-sixth of a carat.

*Bôa Vista* is situated 12 miles east from Diamantina and 8 miles south-west from Serrinha

This high-level diamond-bearing deposit is in many respects similar to the one at Serrinha, except that the sandstone boulders are slightly smaller and a little softer. The cementing material, as far as can be ascertained by present indications, is of the same formation and constituency, but there is a considerable difference in the quality of the diamonds; they are, besides, on an average, smaller and contain a higher percentage of defective stones.

At one time this deposit was worked by a French company, but the then low price of diamonds and the extravagant management led to the inevitable financial failure, and lately a private firm worked the mine by very antiquated methods with satisfactory results. Within the last few months, an Anglo-Brazilian company has purchased the property, and are employing modern methods of extraction with gratifying results.

The area of the diamond-bearing ground is about two square miles. The deepest workings are down to over 100ft., without there being any indications of a change in the formation in the breccia. Tests made of the cementing material indicate that a large part of it was originally composed of olivine. So far, no olivine-bearing rocks have been found in the vicinity, though diligent search has been made in the district; it is, therefore, apparent that the cementing material in the breccia must be derived from some source other than the surrounding rocks.

*Sao Joao do Barro* is situated 20 miles north-west of Diamantina, and 12 miles north-west from Guinda railway station.

This deposit is the highest in the district, being 600ft. higher than the one at Bôa Vista, that is 5000ft. above sea level This deposit in many respects resembles those at Serrinha and Bôa Vista, inasmuch as the breccia consists of angular boulders and slabs of very decomposed sandstone, with a few small pieces of shale and schist, derived from the immediately surrounding rocks. This formation is better defined than at the two above-mentioned localities. The deposit is surrounded on three sides by a well-defined and continuous ring of quartzite.

The area covered by the breccia is about one square mile. The deposit has been tested in several places to 150ft in depth without showing any alteration or change in the minerals contained in the breccia. The cementing material is highly basic, containing talc and magnesia in very large proportions, but owing to the ring of hard quartzite surrounding the deposit, which retains the water collected during the heavy rains, the minerals in the breccia are decomposed to such an extent that they are barely recognisable, and until a greater depth is attained, it will be impossible to determine the various minerals which form the cementing mass.

This deposit has been worked for many years and has yielded the best quality of diamonds of the district. The stones are of a clear blue-white colour, and of good shape, and realise the highest price by weight for local diamonds.

Situated on the extreme eastern edge of the ring of outcropping quartzite is a cutting 1000ft. in length by 300ft. in width, with a depth of 150ft., exposing the different layers forming the last ring or wall of the breccia. The quartzites of the neighbourhood have a dip of from 15° to 20° East, but on the edge of the breccia at this point, the dip is 45° East, thus showing that at some period, local and violent disturbances have taken place, uptilting the strata at such an acute angle.

*Origin of the High-Level Deposits of Diamantina.*—Hitherto these deposits have been described as conglomerates of fluviatile origin, but aqueous conglomerates are totally different from those described at Serrinha, Bôa Vista, and Sao Joao do Barro. In river conglomerates the cementing material filling the interstices between the boulders contains a large percentage of the same material as the boulders themselves, and these consist of various kinds of rocks which are derived from the different strata through which the stream flows. Then again, the boulders are invariably rounded, except those which are derived from the rocks from the immediate vicinity, but the contrary is the case in the above high-level deposits, where the boulders are all of the same rock, whilst the cementing material is of a totally different nature from the boulders. Another cogent reason why these deposits are not of the fluviatile origin is that, in all such gravels and conglomerates, which contain minerals of higher specific gravity than the cementing material, local enrichment takes place, and rich shoots and pockets are formed; this is not so with the deposits in question, where the diamonds are found indiscriminately throughout the cementing mass, and not in patches or pockets. Another and very important point is that, local diamond merchants are able, at a glance, to distinguish parcels of diamonds derived from the various high-level deposits.

It is inconceivable that water could have transported and deposited boulders 1ft or more in diameter and lodged them in a similar mass, and yet regulate the quality of the diamonds to such a nicety that they can be distinguished at a glance.

As the mass contains a considerable amount of olivine, it is obvious that these deposits must be derived from some deep-seated source, either through volcanic or thermal action. The former seems to be the more probable, especially since undecomposed Blue Ground "Kimberlite" has been discovered in Brazil in two different localities many miles apart. This with the above enumerated reasons makes it apparent that these high-level deposits are not conglomerates of fluviatile origin.

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ROYAL INSTITUTION.—At the meeting of March 3, a Discussion on "Isotopes" will be opened by Sir J. J. Thomson, O.M., F.R.S.

## THE PREPARATION OF SELENIUM OXYCHLORIDE.

By VICTOR LENHER.

The first record in the literature that we have of selenium oxychloride is its preparation by Weber in 1859 (Weber, *Pogg. Ann.*, 1859, cviii., 615), who heated together in a knee-shaped tube the vapours of selenium tetrachloride and selenium dioxide. Michaelis prepared the oxychloride by the action of phosphorus pentachloride on selenium dioxide (Michaelis, *Ann.*, 1887, ccxl., 150). Later, in 1889, in their work on selenic acid, Cameron and Macallan mention that selenium oxychloride is formed when common salt is distilled with selenium dioxide (Cameron and Macallan, Chemical News, 1889, lix., 267).

The methods used in this laboratory for the formation of selenium oxychloride may be grouped under three heads.

1. *Direct Union of Selenium Tetrachloride and Selenium Dioxide at Room Temperatures.*

When elementary selenium is suspended in carbon tetrachloride and chlorine gas is passed in, the chlorine first dissolves in the carbon tetrachloride, this being an excellent solvent for chlorine at low temperatures. The dissolved chlorine immediately attacks the selenium, forming selenium monochloride which also dissolves at once in the carbon tetrachloride. Selenium monochloride, in turn, is an excellent solvent for elementary selenium. The solution and chlorination of the selenium is therefore, much expedited.

An alternate method of preparing the two chlorides of selenium which possesses interesting advantages with certain selenium containing materials is to suspend them in carbon tetrachloride, chloroform, or similar solvent, and pass in chlorine. This converts the selenium first to the monochloride which is soluble in carbon tetrachloride while most of the metallic chlorides, being insoluble in carbon tetrachloride, can be at once removed by filtration or decantation, while the further chlorination of the selenium monochloride gives white selenium tetrachloride, which being sparingly soluble, separates out and if de sired can be removed from the solvent by a second filtration.

To the suspended selenium tetrachloride in carbon tetrachloride it is convenient to add the calculated amount of selenium dioxide. Reaction takes place with formation of selenium oxychloride, which dissolves in the carbon tetrachloride. The liquid can then be distilled. Carbon tetrachloride distills at 76-77° and selenium oxychloride at 176·4°, hence they can be readily separated by distilaltion. Selenium oxychloride can be conveniently distilled under diminished pressure to a high degree of purity.

The carbon tetrachloride suggested in the above procedure can be replaced by chloroform or still better replaced by selenium oxychloride itself.

Inasmuch as selenium oxychloride is a solvent for elementary selenium, the entire operation of its formation can be accomplished by mixing together selenium dioxide and elementary selenium, treating this mixture with selenium oxychloride and then chlorinating.

2. *Partial Hydrolysis of Selenium Tetrachloride.*

This can be readily accomplished by treatment with water according to the following reaction.

$$SeCl_4 + H_2O \!-\!= SeOCl_2 + 2HCl.$$

This reaction can be carried out with solid selenium tetrachloride or with the selenium tetrachloride suspended in carbon tetrachloride, chloroform, selenium oxychloride or other liquids.

3. *Dehydration of the Compound $SeO_2 \cdot 2HCl$.*

This substance, first described by Ditte, can be formed by bringing hydrogen chloride into contact with selenium dioxide (*Ann. chim. phys.*, [5] 1877, x., 82). The two substances unite at moderately low temperatures to form an amber-coloured liquid of the formula $SeO_2.2HCl$. It is possible to remove the elements of water from this compound by means of phosphorus pentoxide, calcium chloride, or a similar dehydrating agent. The reaction can be carried out in the laboratory in one of two ways.

Selenium dioxide can be treated with hydrogen chloride, the resulting liquid mixed with excess of the dehydrating agent and the oxychloride distilled off, or selenium dioxide can be first mixed with the dehydrating agent and this mixture treated with hydrogen chloride. The operation can be conducted by either first passing hydrogen chloride into the mixture of selenium dioxide and dehydrating agent in the cold and subsequently heating to drive off the selenium oxychloride formed, or the mixture can be heated, hydrogen chloride passed in, and selenium oxychloride distilled from the hot mixture as it forms.

The author takes this opportunity of acknowledging the valuable help rendered by his assistant, Mr. A. J. Snyder, for various preparations of material in the above processes.—*Journal of the American Chemical Society*, December, 1920.

## THE PREPARATION OF SOME HYDRAZINES.*

By LEONARD THOMPSON, M.Sc. Tech.

The hydrazine compounds were discovered in 1871, in which year Strecker and Römer (*Ber.*, 1871, 784) prepared potassium phenyl hydrazine sulphonate, $C_6H_5NH.NHSO_3K$, by reducing diazobenzene nitrate with potassium bisulphite. E. Fischer (*Ber.*, 1875, 589) hydrolysed this compound and thus obtained phenyl hydrazine. Phenyl hydrazine is generally prepared either by Fischer's method (*Ber.*, 1876, 1331) or by the method of Meyer and Lecco (*Ber.*, 1883, 2976, and 1884, 2972).

In Fischer's method, benzene diazonium chloride is converted into benzene diazosulphonate by pouring the diazo solution into a cold neutral solution of sodium sulphite. The diazo-sulphonate is most conveniently reduced by means of zinc and acetic acid. The solution of phenyl hydrazine sulphonic acid thus obtained is hydrolysed by hot concentrated hydrochloric acid, the phenyl hydrazine hydrochloride then being isolated and treated with caustic soda to give the free base. The yield of purified base is 60-65 per cent.

In Meyer's method a strong solution of benzene diazonium chloride is added to a cooled solution

* Read before the Manchester Section of the Society of Dyers and Colourists, November 19, 1920.

of excess of stannous chloride in concentrated hydrochloric acid. The tin double salt of phenyl hydrazine hydrochloride separates, from which the base is obtained by treatment with caustic alkali. The maximum yield stated is 85 per cent.

*Phenyl hydrazine p-sulphonic acid.*—This technically important derivative was first prepared by Strecker and Romer (*Ber.*, 1871, 784) by treating diazotised sulphanilic acid with potassium bisulphite and hydrolysing the resulting hydrazine sulphonate with hydrochloric acid. This method substituting sodium bisulphite, however, is used technically (*Annalen* 278, p. 297). Stannous chloride also brings about the reduction (*Ber.*, 1889, ref. 216), and sodium amalgam may be used to reduce the sodium iso-diazo salt (*Ber.*, 1897, 218). This hydrazine compound is also produced readily with quantitative yield by sulphonating phenyl hydrazine (*Ber.*, 1885, 3172; cf. also E. Fischer, *Annalen*, 1878, p. 76).

*Para-nitro phenyl hydrazine.*—This is one of the most useful of the hydrazine compounds and is largely replacing phenyl hydrazine itself, and the *p*-bromo derivative, for the preparation of characteristic derivatives of aldoses and ketoses owing to its stability and the greater crystallising power of its derivatives. *p*-Nitro phenyl hydrazine was first obtained by Purgotti (*Ber.*, 1892, 119), who used sodium bisulphite as the reducing agent. The general method of preparation is that of Bamberger and Kraus (*Ber.*, 1896, 1829), in which the neutralised concentrated diazo solution is poured into excess of neutral potassium sulphite, when *p*-nitro phenyl hydrazine disulphonate of potassium is produced. This is isolated, hydrolysed with hydrochloric acid, and the hydrazine base obtained by treatment with sodium carbonate and sodium acetate. The yield is given as almost quantitative.

Sodium sulphite may be used instead of the potassium salt, the method being described by Cohn (*Die Pyrazolfarbstoffe*), but this has several disadvantages.

*Meta-nitro phenyl hydrazine.*—This hydrazine derivative was first prepared and described by Bischler and Brodsky (*Ber.*, 1889, 2809), who obtained it by the reduction of meta-nitro benzene diazonium chloride with stannous chloride. The tin double salt of *m*-nitro phenyl hydrazine hydrochloride is produced, which is freed from tin by means of hydrogen sulphide. Yield, 50-60 per cent. The free base is obtained by treatment with sodium acetate.

The preparation by the sulphite method does not appear to have been fully investigated (see Hantzsch and Borghaus, *Ber.*, 1897, 89).

The hydrazine compounds enumerated above include the more important members of a class of compounds having numerous practical applications. Thus they are used in the manufacture of dyestuffs of the Tartrazine class, and in the identification and quantitative estimation of certain aldehydes and ketones, especially the carbohydrates. *p*-Nitro phenyl hydrazine has also been found to be a very useful reagent for the identification of oxycellulose, though it has been proved to be useless for the quantitative estimation of this substance. It was with a view to its use for this purpose, however, that the present work was undertaken In view of the results already published (*Journ. Soc. Dyers and Colourists*, Aug., 1920) on the estimation of diazo compounds by reduction to the corresponding hydrazine compound, it was thought desirable to try other reducing agents, and of these sodium hydrosulphite and titanous chloride have been experimented with.

It is now found that phenyl hydrazine hydrochloride can be readily prepared directly by the reduction of benzene diazonium chloride with sodium hydrosulphite in presence of hydrochloric acid, according to the equation—

$$C_6H_5N_2Cl+2Na_2S_2O_4+4H_2O = C_6H_5NH.NH_2.HCl+4NaHSO_3.$$

If solid sodium hydrosulphite be used for the reduction, the reaction is not quantitative, a small quantity of bright red compound being formed. This is presumably azo benzene *p*-hydrazine sulphonic acid, as observed by Grandmougin (*Ber.*, 1907, 858), who obtained in addition, a large proportion of diazoimides and sulphones, as well as the hydrazine sulphonate when carrying out this reduction with hydro-sulphite under different conditions.

The preparation of phenyl hydrazine can be carried out by using only one molecule of hydrosulphite, in which case the first product is phenyl hydrazine sulphonate of sodium. Besides being the cheaper process, this method gives a higher yield, as the volume of the solution is kept down to a minimum.

18·6 grms. of aniline are treated with 55 cc. of concentrated hydrochloric acid and 50 grms. of ice. The paste of aniline hydrochloride is cooled in a freezing mixture and diazotised with a cooled solution of 15 grms. of sodium nitrite in 30 cc. of water, a clear diazo solution being thus obtained. 46 grms. of hydrosulphite (80 per cent) is dissolved in 250 cc. of water containing a few drops of caustic soda to prevent decomposition, the solution being prepared in a stoppered flask of 250-300 cc. capacity. Both solutions are cooled to 0° C.; 20 cc. of concentrated hydrochloric acid is added to the diazo solution, and the hydrosulphite solution is then added fairly rapidly to the well-stirred diazo solution. Complete reduction takes place immediately, sulphur dioxide is evolved, and some of the hydrazine sulphonate is precipitated. 100 cc. of concentrated hydrochloric acid is added, and the solution boiled for a few minutes. A colourless solution of phenyl hydrazine hydrochloride is obtained, from which, on cooling to 0° C., the hydrochloride separates as a mass of white needle-shaped crystals. This is filtered off, pressed, and dried. Yield, 24·5 grms. (85 per cent of the theoretical).

A further quantity can be obtained from the mother liquor by adding a large quantity of concentrated hydrochloric acid. The mixture of the hydrazine hydrochloride and common salt which separates is removed by decantation and gives, on treating with caustic soda and extracting with ether, a further 1·5 grm. of the base (7 per cent theoretical). Alternatively the mother liquor may be rendered alkaline with strong caustic soda solution and extracted with ether, giving a further 5 per cent yield of the base. Hence a yield of over 90 per cent of the hydrazine is obtained by this method. The free base can be obtained from the hydrochloride in the ordinary way by shaking with 10-20 per cent caustic soda and extracting several

times with ether. The ethereal solution is dried with potash, filtered, freed from ether by distillation, and purified by distillation under reduced pressure.

The hydrosulphite reduction process has certain advantages over the methods of reduction in use. Sodium bisulphite is not a sufficiently strong reducing agent to bring about the reduction to hydrazine sulphonate readily, hence Fischer used zinc and acetic acid as the reducing agent, but this cannot be used without first forming the diazo sulphonate. Hence a somewhat more energetic reducing agent than bisulphite, which moreover affects the reduction directly, is preferable, especially as there is no risk of further reduction occurring at the hydrazine group. As compared with V. Meyer's process, the hydrosulphite method has the advantage of giving pure phenyl hydrazine hydrochloride, whereas in the former method practical difficulties are introduced by the presence of tin. The hydrosulphite process gives a better yield than either of the other methods

The reactions are represented by the following equations—

$$C_6H_5N_2Cl+Na_2S_2O_4+H_2O = C_6H_5NH.NHSO_3Na+NaCl+SO_2.$$

$$C_6H_5NH\ NHSO_3Na+HCl+H_2O = C_6H_5NH.NH_2.HCl+NaHSO_4.$$

*Phenyl hydrazine p-sulphonic acid.*—This can be readily prepared by a method similar to that used for preparing phenyl hydrazine, employing either one molecule or two molecules of hydrosulphite. In the latter case the hydrazine is obtained directly with a yield of about 53 per cent. Using one molecule of reducing agent the method is as follows: The solid diazo anhydride is first prepared by dissolving 19 grms. of recrystallised sulphanilic acid in 23 cc. of 20 per cent caustic soda and 100 cc. of water. Seven grms. of sodium nitrite are added, and the solution is poured into a cold solution of 12 cc. of strong sulphuric acid in 100 cc. water. The precipitated diazo compound is filtered off. The diazo compound in the form of a paste is reduced with a cooled solution of 22 grms. of hydrosulphite in 125 cc. of water, 20 cc. of hydrochloric acid being added during the reduction. The clear yellow solution of the *p*-sulphonic acid of phenyl hydrazine sulphonate of sodium which is thus produced, is easily hydrolysed by boiling with a further 30 cc. of hydrochloric acid. The free hydrazine is obtained directly as this hydrazine derivative forms no hydrochloride; 8·5 grms. of the pure base are obtained on crystallising, and the mother liquor gives a further 3 grms. on boiling down. This gives a total yield of 60 per cent of the theoretical, calculated on the original amine.

$$C_6H_4\left\langle\begin{matrix} N:N \\ SO_3 \end{matrix}\right/ +Na_2S_2O_4+HCl+H_2O = SO_3H.C_6H_4NH.NHSO_3Na+NaCl+SO_2.$$

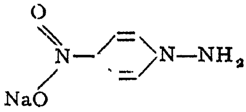
$$SO_3HC_6H_4N_2H_2SO_3Na+H_2O = SO_3H.C_6H_4NH.NH_2+NaHSO_4.$$

It is interesting to note that the theoretical quantity of reducing agent is employed, whereas in the ordinary method about 2½ times the theoretical quantity of bisulphite is generally used.

*Para-nitro phenyl hydrazine.*—The reduction of *p*-nitro benzene diazonium chloride with hydrosulphite does not give satisfactory results under the conditions given above, or, indeed, under any of our experimental conditions. This is due to several factors. *p*-Nitro phenyl hydrazine differs from the hydrazines already dealt with in being further reducible both at the hydrazine group and the nitro group the ultimate reduction product being *p*-phenylene diamine. Consequently, the sulphonic groups cannot be removed from the hydrazine disulphonate by the further action of hydrosulphite. Moreover, it is not theoretically possible to prepare the hydrazine disulphonate by the action of hydrosulphite alone, whether the latter goes to sulphite or sulphate, and there is no monosulphonate. Furthermore, the product of the reduction always resinifies, thus accounting for the presence of unreduced diazo sulphonate. The best yield of hydrazine was obtained under the following conditions: 42 grms. of *p*-nitraniline were boiled with 200 cc of water and 100 cc. of concentrated hydrochloric acid, and the solution cooled in a freezing mixture. This was diazotised at a low temperature by rapidly adding 24 grms. of sodium nitrate dissolved in 50 cc. of water. The filtered diazo solution was treated with 30 cc. of concentrated hydrochloric acid, stirred mechanically, and slowly reduced at a temperature not exceeding 2° C. with 130 grms. of hydrosulphite dissolved in 700 cc. of water. The solid product contained both the hydrazine hydrochloride and hydrazine disulphonate, and gave 13 grms. of the hydrazine base after hydrolysing and treating with sodium carbonate and sodium acetate. The mother liquor gave 6 grms. of the base on neutralising, and after salting out the remaining hydrazine disulphonate, this gave a further 4 grms. of the base. By extracting with ether a further small quantity was obtained. This makes a total yield of 24 grms. or 53 per cent of the theoretical.

When the reduction is carried out in sodium carbonate solution, the main product appears to be *p*-nitro diazo benzene imide.

*Para*-nitro phenyl hydrazine can, however, be prepared by reduction of sodium *p*-nitro isodiazo benzene with hydrosulphite in alkaline solution, the method being similar to that used for the estimation of this diazo or nitrosamine compound. The product is a tautomeric form of *p*-nitro phenyl hydrazine which is supposed to have a quinonoid structure and forms a sodium salt, as shown by Baly and Tuck (*J. Chem. Soc.*, 1906).



This gives the ordinary hydrazine on neutralising with acid. The product obtained in this preparation consists of a mixture of *p*-nitro phenyl hydrazine with a small proportion of the hydrazine disulphonate. It is best to isolate the nitrosamine compound and to carry out the reduction fairly rapidly so as to minimise the proportion of hydrazine disulphonate formed. Under certain conditions the product is obtained on neutralising in a finely divided form which is difficult to isolate. This is obviated if the acid hydrolysis is carried out as described below without isolating the hydrazine. The production of hydrazine compound was shown by titrating the solution resulting from this preparation to be practically quantitative.

THE

# CHEMICAL NEWS

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IN ALL ITS APPLICATIONS TO

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# INDEX.

END OF VOLUME CXXI.

The nitrosamine compound is obtained by pouring the diazo solution into caustic soda, as described by Schraube and Schmidt (*Ber.*, 27, 514).

Ten grms. of the pure nitrosamine compound, $NO_2C_6H_4N_2ONa,2H_2O$, was mixed with a little water containing 6 grms. of caustic soda and reduced at 0° C. with 20 grms. of hydrosulphite dissolved in 120 cc. of water. Some of the hydrazine base crystallised out as the quantity of alkali was only slightly in excess of that required by the equation :

$$NO_2C_6H_4N_2ONa+2Na_2S_2O_4+3NaOH= NO_2C_6H_4N_2H_3+4Na_2SO_3.$$

200 cc. of hydrochloric acid was added and the solution boiled, in order to hydrolyse the small quantity of hydrazine sulphonate present. On neutralising the cooled solution with sodium carbonate and sodium acetate, 6·2 grms. of *p*-nitro phenyl hydrazine was obtained. Ether extraction of the mother liquor gave a further 0·3 grm. of the base. The total yield is 95 per cent of the theoretical.

*Meta-nitro phenyl hydrazine.*—The action of hydrosulphite on *m*-nitro benzene diazonium chloride under various conditions was investigated with the object of preparing *m*-nitro phenyl hydrazine. The reduction is analogous to that of the *p*-nitro compound, but only comparatively low yields of the hydrazine (40 per cent) were obtained, together with the hydrazine disulphonate, the diazo sulphonate, and, when working in sodium carbonate solution, the diazo imide.

*Use of titanous salts for the reduction of diazo compound.*—It has been stated in a previous paper that phenyl hydrazine is not obtained by the action of titanous salt on benzene diazonium chloride, the product being diazo benzene phenyl hydrazide, which is a condensation product of the diazo compound with phenyl hydrazine. In the case of diazotised *p*-nitraniline a similar reaction probably occurs, as only about half the theoretical quantity of reducing agent is used up. By carrying out the reduction with this reduced quantity of titanous sulphate, a bulky red precipitate was obtained which was extracted with alcohol and treated with sodium carbonate. The product thus obtained was free from titanium and contained no diazo imide. It was insoluble in cold water, decomposed by hot water, and melted at 65-70° C. By treating with alcoholic potash or alkaline hydrosulphite and then acidifying, *p*-nitro phenyl hydrazine was formed. Hence the substance was probably a diazo hydrazide, and although the compound $NO_2C_6H_4N : N.N(NH_2)C_6H_4NO_2$ has not been previously described, Bamberger (*Ber.*, xxviii., 840) obtained a very similar compound of the formula $NO_2C_6H_4N : N.N.(NH_2)C_6H_4$.

It has now been found that analogous reactions take place when stannous chloride and bisulphite of soda are used as reducing agents, the equivalent of only one molecule (=2H instead of 4H) of either of these being sufficient to prevent the coupling of a solution of diazotised *p*-nitraniline with β-naphthol. These results have some bearing on the method of producing white resists under insoluble azo colours in calico printing. In the printing of stannous chloride and bisulphite resists on β-naphthol prepared cloth under diazotised *p*-nitraniline or α-naphthylamine, it is generally assumed that the diazo compounds do not touch the printed parts owing to their being instantly reduced to hydrazine compounds. This evidently does not take place, and the fact that no colour develops is due to other causes. Presumably in the case of diazotised *p*-nitraniline, a precipitate of the insoluble diazo hydrazide is immediately formed where the diazo compound comes in contact with the stannous chloride. Furthermore, the stannous chloride used is capable of destroying, as far as the coupling effect is concerned, twice as much of the diazo compound as if it brought about the reduction to the ordinary hydrazine.

In the case of diazotised meta-nitraniline, a similar reaction apparently occurs, but here the diazo hydrazide is further reducible either by titanous or stannous salts, and it has therefore been possible to prepare *m*-nitro phenyl hydrazine by using titanous sulphate as reducing agent. The product of the reduction is a yellowish-orange frothy precipitate, which is remarkably bulky. After filtering and extracting with hot alcohol, the alcoholic solution gives a flocculent precipitate of what appears to be the titanium double salt of *m*-nitro phenyl hydrazine. Such double salts of titanium with a salt of an organic base are very rare, and an attempt was made to purify some of this as the oxalate, but it could not be obtained crystalline. The free hydrazine base was obtained from the solution of the double salt by treating with sodium acetate, boiling, and filtering from the residue of titanic hydrate. The yield of the base thus obtained is 65 per cent of the theoretical. This method of preparation does not seem to be of much value, owing to the practical difficulties which are encountered.

Thus it is evident that sodium hydrosulphite can be used with advantage in the preparation of hydrazine derivatives, in place of bisulphites and stannous salts, which have formerly been almost invariably used. In certain cases titanous salts may be used for the purpose, but do not offer any advantages In conclusion, I wish to thank Prof. Knecht for his direction and supervision of this work.

## THE CHEMISTRY AND CRYSTALLOGRAPHY OF SOME FLUORIDES OF COBALT, NICKEL, MANGANESE AND COPPER.*

By FLOYD H. EDMINSTER and HERMON C. COOPER.

(Continued from p. 30.)

*Cobalt Fluoride Analysis.*—The fluorine of the cobalt fluoride was determined by adding an excess of standard alkali to the water solution. The precipitate was four times washed by decantation with hot water, whereupon it was brought upon the filter and washed with hot water until the washings gave no test for alkali with phenolpthalein. The filtrate was then titrated with standard hydrochloric acid and the weight of sodium hydroxide used was calculated. In order to check this method, determinations were made by precipitating the fluorine with calcium acetate. The results were lower than by titration, and are not considered reliable.

*A more detailed account of this work was submitted to the Faculty of the Graduate School of Syracuse University by Floyd H. Edminster in May, 1918, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

All of the general methods were used for determining cobalt metal. The first method employed was that of precipitating with sodium hydroxide, filtering the precipitate, and washing it with hot water. The dried hydroxide was ignited and the oxide decomposed with concentrated sulphuric acid. This acid solution was then evaporated to dryness and the anhydrous cobalt sulphate weighed.

Another method used for cobalt was to treat the fluoride with sulphuric acid and evaporate. This should volatilise all of the constituents except the metal. Consistent results were obtained by this method which agree with the electrolytic determinations. The reaction with sulphuric acid is vigorous and complete within a few minutes. The sulphuric acid is then driven off in an air-bath, the residue heated for five minutes and eventually weighed as anhydrous cobalt sulphate.

In electrolytic deposition, cobalt does not behave ideally; it does not always form a good coating on the cathode, but often scales off before the deposition is complete. We carried out the electrolysis as specified by Treadwell-Hall (Treadwell-Hall, "Analytical Chemistry" II., 1915, p. 138, 4th ed., N.Y.). Our experience has been that, if the voltage exceeds 1·5 volts, the cobalt will precipitate as the hydroxide, and, if the solution is not kept strongly alkaline, a black ring will be deposited, particularly around the edge. A voltage of 1·0 to 1·5 and an amperage of 1·0 to 1·3 gave the best results. A 100-cc. platinum basin served as the cathode. It is not necessary to precipitate the hydroxide of cobalt, but the crystals may be dissolved in water, ammonium hydroxide added, and the solution electrolysed directly. The possibility of contamination with alkali is eliminated and accurate results are to be expected, but no determination of fluorine can be made on the same sample.

Cobalt hydroxide was also reduced to the metal by the Rose method. Unfortunately, the ignited precipitate was always in masses, which would not reduce unless removed from the crucible and ground. If this was not done, the reduction was incomplete, and the results were too high.

*Nickel Fluoride Analysis.*—In the nickel fluoride the fluorine was determined as in the case of cobalt. The metal also was determined (1) as the anhydrous sulphate, after evaporating the fluoride crystals with sulphuric acid; (2) by electrolysis; and (3) as the oxide. Unlike cobalt oxide, nickel oxide has a constant composition and the metal can be calculated from the weight of the oxide.

Anhydrous nickel sulphate is hygroscopic and must be weighed quickly after removal from the desiccator. The electrolysis was conducted in a strongly alkaline solution with a voltage of about 1·5 and an amperage of 1·5. In all cases the platinum basin was used as the cathode.

No analyses for nickel were made by the Rose method.

*Copper Fluoride Analysis.*—The copper is best determined (1) by electrolysis in the water solution of the crystals, which are acid with hydrofluoric acid, unless the fluorine is to be determined in the same sample. In the latter case, the copper is precipitated as the hydroxide, dissolved in dilute nitric acid, and subjected to electrolysis. Copper was also determined (2) by evaporating the crystals with sulphuric acid. (3) When the copper fluoride crystals are heated alone, they give off water and hydrofluoric acid and are converted to the oxide. The weight of copper calculated from the oxide thus obtained agrees approximately with that obtained by other methods.

*Manganese Fluoride Analysis.*—The fluorine was determined by the same method as for the other fluorides. The metal was determined (1) by decomposing with sulphuric acid, and (2) by converting to the pyrophosphate. For the latter method the manganese is first precipitated as the hydroxide, washed free from alkali and dissolved in dilute sulphuric acid.

*The Analytical Data.*—The results of the analyses are tabulated in the following tables. The numbers in the first column are analytical reference numbers; the method employed in the analysis is indicated in the second column; the weights of salt and constituent, respectively, are given in the next two columns; the computed percentage is found in the fifth column; while below will be found memoranda that might aid in the appraisal of the results.

*Cobalt Fluoride.*

Prepared by the action of HF on the hydroxide or carbonate, no difference being seen in the products.

| Reference No. | | Salt G. | Fluorine. G. | Per cent. |
|---|---|---|---|---|
| 6 | Pptd. as $CaF_2$ ... | 0·3000 | 0·1214 | 39·97 |
| 3 | Titration ... ... | 0·5000 | 0·1310 | 41·30 |
| 63 | Titration ... ... | 0·3000 | 0·1221 | 40·78 |
| 64 | Titration ... ... | 0·4007 | 0·1605 | 41·45 |
| 90 | Titration ... ... | 0·3000 | 0·1285 | 42·85(a) |
| 130 | Pptd. as $CaF_2$ + $CaC_2O_4$ ... ... | 0·2934 | 0·1458 | 42·79(a) |
| 131 | Pptd. as $CaF_2$ + $CaC_2O_4$ ... ... | 0·2280 | 0·1232 | 43·79(a) |

(a) Taken from solution, washed, dried, and analysed immediately.

| Reference No. | | Salt. G. | Metal. G. | Per cent. |
|---|---|---|---|---|
| 37 | Dissolved hydroxide in $H_2SO_4$ and electrolysed .. | 0·3026 | 0·0591 | 19·53(a) |
| 39 | Dissolved hydroxide in $H_2SO_4$ and electrolysed ... | 0·4483 | 0·0864 | 19·27 |
| 50 | Decomposed with $H_2SO_4$ and weighed as $CoSO_4$ ... | 0·3520 | 0·1793 | 19·36 |
| 63 | Electrolysis ... | 0·3000 | 0·0571 | 19·40 |
| 78 | Electrolysis ... | 4·4007 | 0·7840 | 19·40(b) |
| 93 | Electrolysis ... | 0·3000 | 0·0590 | 19·60(c) |
| 51 | Electrolysis ... | 0·2544 | 0·0484 | 19·03(d) |

(a) Crystals were washed in alcohol.
(b) Very clean crystals.
(c) Dissolved in water and electrolysed.
(d) Dehydrated.

| Reference No | | Salt. G | Metal. G. | Per cent. |
|---|---|---|---|---|
| 51 | Heating and collecting the water | 0·2544 | 0·1036 | 40·70 |
| 130 | Heating and collecting the water | 0·3024 | 0·1195 | 39·52 |
| 133 | Heating with PbO | 0·3313 | 0·1363 | 41·14 |
| 135 | Heating with PbO | 0·1853 | 0·7440 | 41·15 |
| 137 | Heating and collecting the water | 0·2107 | 0·8650 | 41·05 |

### *Nickel Fluoride.*

Prepared from the hydroxide and hydrofluoric acid.

| Reference No. | | Salt. G. | Fluorine. G. | Per cent. |
|---|---|---|---|---|
| 58 | Titration ... .. | 0·3000 | 0·1259 | 41·99(a) |
| 80 | Titration ... ... | 0·3000 | 0·1658 | 41·36(b) |
| 89 | Titration ... ... | 0·3000 | 0·1296 | 43·27(c) |
| 96 | Titration ... ... | 0·3000 | 0·1292 | 43·05(d) |
| 97 | Titration . . ... | 0·3000 | 0·1248 | 41·67(e) |
| 131 | Pptd. as $CaF_2$+ $CaC_2O_4$ ... ... | 0·1876 | 0·0914 | 43·76 (f) |

(a) Washed in alcohol.
(b) Old crystals.
(c) Clean crystals fresh from solution.
(d) Clean crystals fresh from solution
(e) Old crystals
(f) Crystals fresh from solution.

| Reference No. | | Salt. G | Metal. G. | Per cent. |
|---|---|---|---|---|
| 54 | Electrolysis ... | 0·3070 | 0·0677 | 19·80 |
| 58 | Electrolysis ... | 0·3000 | 0·0584 | 19·60 |
| 62 | Electrolysis . | 0·3000 | 0·0574 | 19·50 |
| 64 | Electrolysis ... | 0·2497 | 0·0489 | 19·58 |
| 91 | Electrolysis ... | 0·3000 | 0·0478 | 19·26 |

| Reference No. | | Salt. G. | Water. G. | Per cent. |
|---|---|---|---|---|
| 110 | Heating and collecting water in $H_2SO_4$ ... . . | 0·2764 | 0·1149 | 41·50 |

### *Manganese Fluoride.*

| Reference No | | Salt. G. | Fluorine. G. | Per cent. |
|---|---|---|---|---|
| 76 | Titration ... ... | 0·3537 | 0·1313 | 43·02(a) |
| 69 | Titration ... ... | 0·3004 | 0·1190 | 39·63 |
| 92 | Titration ... ... | 0·3020 | 0·1220 | 40·68 |

(a) Crystals fresh from solution.

| Reference No. | | Salt. G. | Metal. G. | Per cent. |
|---|---|---|---|---|
| 76 | Heating with $H_2SO_4$ and weighing as $MnSo_4$ ... ... | 0·0365 | 0·1817 | 18·09 |
| 60 | Heating with $H_2SO_4$ and weighing as $MnSO_4$ ... ... | 0·3537 | 0·1810 | 18·89 |
| 77 | Heating with $H_2SO_4$ and weighing as $MnSO_4$ ... ... | 0·2892 | 0·1457 | 18·35 |

| Reference No. | | Salt. G | Water. G. | Per cent. |
|---|---|---|---|---|
| 127 | Heating with PbO and collecting the water ... ... | 0·3171 | 0·1221 | 38·2 |

### *Copper Fluoride (Crystals).*

| Reference No. | | Salt. G. | Fluorine. G. | Per cent. |
|---|---|---|---|---|
| 43 | Titration ... ... | 0·3000 | 0·1282 | 42·76 |
| 59 | Titration ... ... | 0·3000 | 0·1281 | 42·71 |
| 65 | Titration ... ... | 0·4220 | 0·1808 | 43·05 |
| 127 | Precipitation ... | 0·3612 | 0·1519* | 42·20 |

* $CaF_2+CaC_2O_4$

| Reference No. | | Salt. G. | Metal. G. | Per cent. |
|---|---|---|---|---|
| 59 | Electrolysis ... | 0·3000 | 0·0610 | 20·30 |
| 60 | Electrolysis ... | 0·3000 | 0·0602 | 20·07 |
| 61 | Electrolysis ... | 0·3009 | 0·0604 | 20·06 |
| 79 | Electrolysis ... | 0·4112 | 0·0838 | 20·38 |

### *Copper Fluoride (Crystalline Crust).*

| Reference No. | | Salt G | Fluorine. G. | Per cent. |
|---|---|---|---|---|
| 52 | Titration ... ... | 0·6087 | 0·1692 | 27·80(a) |
| 53 | Titration . .. | 0·6896 | 0·1270 | 27·00 |
| 56 | Titration ... ... | 0·5000 | 0·1437 | 28·75 |
| 74 | Titration ... ... | 1·1751 | 0·3323 | 28·28 |
| 83 | Titration ... ... | 0·9401 | 0·2646 | 28·13 |

(a) These two are the same preparation.

| Reference No. | | Salt G | Metal. G | Per cent. |
|---|---|---|---|---|
| 52 | Electrolysis .. | 0·0609 | 0·2814 | 46·10 |
| 53 | Electrolysis ... | 0·6896 | 0·3158 | 45·80 |
| 82 | Electrolysis ... | 0·8219 | 0·3767 | 45·83 |
| 83 | Electrolysis ... | 0·9401 | 0·4306 | 45·82 |
| 49 | Electrolysis ... | 0·3621 | 0·1643 | 45·40 |

(To be continued.)

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

*Ordinary Meeting, January 20, 1921.*

PROF. C. S. SHERRINGTON, President, in the Chair.

THE following papers were read :—

"*The Magnetic Mechanical Analysis of Manganese Steel.*" By Sir ROBERT HADFIELD, S. R. WILLIAMS, and I. S. BOWEN.

This paper is an attempt to correlate some of the magnetic and mechanical properties of manganese steel. Tests were made on six rods quenched in water, when they are in the non-magnetic condition, and three were afterwards annealed, which renders them magnetic. The changes in length of the rods when subjected to magnetic fields were determined (Joule Effect). In the case of the rods in the magnetic condition the change was an increment for all field strengths. No change in length to 0·000004 cm. could be detected for the non-magnetic specimens.

The effect on the intensity of magnetisation when subjected to longitudinal stress was investigated (Villari Effect). An absolute method of measuring the intensity of magnetisation when comparatively small was adopted, consisting in the use of an exploring coil made up of two coils in series so arranged that the E.M.F. generated in the first balances that in the second, and calibrated by means of a long solenoid of general dimensions equal to those of the rods tested. For all field strengths the application of tensile stress increased the intensity of magnetisation of the magnetic specimens.

The non-magnetic rods showed no change in intensity of magnetisation by being stretched. They did, however, show an intensity of magnetisation about 1/36 of that of the specimens in the magnetic condition. This effect was found to be entirely due to oxidation of the skin of the rods, for, on removing a few thousandths, the specimens showed no magnetic susceptibility when tested by a hand magnet.

"*A Selective Hot-wire Microphone.*" By W. S. TUCKER, D.Sc., and E. T. PARIS.

The instrument consists of an electrically heated grid of fine platinum wire placed in the neck of a Helmholtz resonator. The effect of a sound

having the same frequency as that natural to the resonator itself is to produce an oscillatory motion of the air in the neck of the resonator, which in turn causes changes in resistance of the platinum wire grid. The total resistance change comprises a steady fall in resistance, due to an average cooling of the grid and a periodic change due to the to-and-fro motion of the air.

Two methods of using the microphone are described :—

(i.) A Bridge method, depending on the steady drop in resistance, and

(ii.) An Amplifier method which makes use of the periodic resistance changes.

Curves are given showing the sharpness of resonance a smeasured by the Bridge method. The various factors affecting the sensitivity of the microphone are discussed.

Results of experiments on cooling the grid by low-velocity air-currents are described. It is deduced that the principal resistance changes to be expected when the grid is cooled by an oscillatory air-current are :—

(1) A steady drop due to an average cooling;

(2) A periodic resistance change of the same frequency as that of the sound; and

(3) A periodic resistance change of frequency twice that of the sound.

All these effects are found in practice. Further deductions are that the steady change of resistance is proportional to the *intensity* of the sound, while the periodic resistance change in (2) is proportional to the *amplitude*. These conclusions are confirmed by experiment.

"*Siren Harmonics and a Pure-tone Siren.*" By E. A. Milne and R. H. Fowler.

The ordinary siren can be regarded as a point source of air variable flux, the flux being proportional to the area of the orifice exposed by the holes in the disc. In general the tone from such a siren is far from pure.

The relative intensities of the harmonics for a siren with circular holes and a circular orifice are calculated and compared with experiment. It is concluded that a fairly pure note should be obtained from a siren of this type, in which the distance between the centres of adjacent holes is twice the diameter of the holes.

If, however, the original is rectangular in section, the holes can be so shaped that the area of the orifice exposed varies exactly as the sine of the displacement. Such a siren should produce a very pure tone.

Experimental tests of a siren constructed on these lines are quoted and discussed.

"*Design of Diaphragms capable of Continuous Tuning.*" By L. V. King.

In designing submarine sound generators and receivers it is important to be able to tune the diaphragm to a desired pitch, thus realising selective transmission and reception.

A type of diaphragm so constructed that continuous tuning is achieved by the application of air-pressure (or suction) was designed by the writer and is designed in detail. It is constructed from a single piece of metal, and consists of a thick, undeformable, central disc, connected by a thin, concentric, annular portion, to a heavy circular rim, which is fited very accurately on a rigid mounting. The application of air-pressure over the interior of the diaphragm alters the tension of the thin annular portion, so that the rigid central portion vibrates about the static equilibrium position with a different pitch.

A steel diaphragm, 3in. in diameter, was constructed in the manner described. A range of pressure from —25cm. of mercury to +25 cm. altered the pitch of the diaphragm vibrating in air from 430 to 620, and vibrating in water from 370 to 530.

By comparing the frequencies corresponding to the same pressures on the diaphragm when vibrating in air and water, it is shown that the *accoustic mass* amounted to as much as 40 per cent of the actual mass.

To realise sharp tuning and high sensitivity, it was concluded as a result of experience that diaphragms of this type should be made with almost optical precision in the form of accurate solids of revolution.

## CORRESPONDENCE.

### GLUCOSAZONE SULPHURIC ACIDS.

*To the Editor of the Chemical News.*

Sir,—While the glucosazones are well-known compounds, their sulphuric acids do not seem to have been prepared and described.

A short investigation of these bodies was undertaken early in 1920, with the following results.

(1) Sodium phenylglucosazone para sulphurate was prepared by heating phenylhydrazine para sulphuric acid with glucose and sodium acetate in aqueous solution: it was obtained as a pale lemon yellow powder, very soluble in water, slightly soluble in absolute alcohol, and insoluble in ether, acetone, benzene, &c. I have not succeeded in crystallising it.

(2) Sodium phenyllactosazone para sulphonate was prepared in the same way, and has similar properties.

(3) Sodium naphthylglucosazone 1 : 4 sulphonate was obtained in a similar way from naphthylhydrazine 1 : 4 sulphuric acid (prepared from naphthianic acid): it is a powder similar to the above, though not such a pure colour.

These osazones are dyes similar to phenyl glucosazone para carboxylic acid described by Kodak, Ltd., in the *British Journal of Photography* in 1919.

It is clear that by the use of halogen and other derivatives of phenyl and naphthylhydrazine sulphuric acids many new osazones could be prepared; also various sugars and substances such as glycerine aldehyde which contain the group —CHOH—CHO might be employed.

Since one molecule of a sugar combines with two of a hydrazine derivative to form an osazone, it seems to me probable that two further series of compounds could be prepared; (*a*) where one molecule of a sugar combines with one molecule of a dihydrazine derivative obtained from diamines such as phenylene and toluylene diamines;

(*b*) where one molecule of a sugar combines with *one* molecule of a dihydrazine derivative obtained from benzidene, tolidine, &c.

I think that some of these new osazones would be likely to prove of considerable interest, and possibly also of value as dyes. Lack of time has so far prevented my preparing more than the three compounds above mentioned.—I am, &c.,

A. F. Kitching (M.A. Oxon.).

Monkton Combe School,
Near Bath.

## NOTES.

Anhydrous Sulphates and the Theory of the Magneton.—When a substance in the form of gas or solution obeys the law of Curie, a single measurement at the ordinary temperature enables determination of the atomic moment. Such is not so when the paramagnetic salts are solid. Study of the thermic variation then becomes essential to determine by means of the Curie point, the constant of the molecular field. The experiments of M. Théodoridès dealt with the three manganous cobaltous and ferric sulphates in the anhydrous form and the method employed was that of the attraction in a non-uniform field with electrodynamic compensation of the magnetic force exerted. For each of the three substances studied, the inverse of the specific coefficient of magnetisation, in function of the temperature, is given by two parallel lines, with a slight intervening deviation, and united by a faint curvilinear region; the ensembling the phenomenon is exactly reversible. Finally the error in calculation of the molecular constant did not attain 6 per 1000; it is reduced to half this figure when estimating the number of magnetons.—*Comptes Rendus*, November 15, 1920.

Purification of Sewage by the "Activated Sludge" Process.—We are aware that in aërating sewage sludge by blowing air through it, this sludge will after a certain time acquire the faculty of purifying the sewage with which it is in contact. Aëration being sufficiently maintained, purification is obtained in a few hours, provided that the proportion of the mixture is suitable. As soon as activity appears there is a sudden fall of ammonia which is found in form of nitrous and nitric acid. M. Cavel describes his experiments in this note and maintains that this transformation of ammonia is a microbial phenomenon. Experiments were made in an alkaline medium which is the normal reaction of sewage. If we change the reaction by slightly acidulating, the action is no longer the same, there is no change in the ammonia; percentage remains constant which is in harmony with what is known regarding the sensitiveness of nitrobacters with regard to acidity of the medium—*Comptes Rendus*, January 8, 1921.

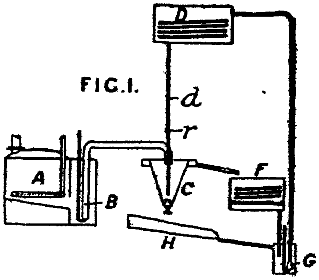
## New Patents.

This List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W.C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Abstract Published this Week.*

Mr R. Lessing of High Holborn, London, has obtained a Patent for apparatus for treating Ammonium Sulphate No. 152766. The colouring matter usually associated with crystals of ammonium sulphate is removed by agitating the latter, in a detached condition in a clear saturated solution of that salt maintained slightly acid—if necessary by the addition of sulphuric acid—and floating of the suspended impurities. The agitation may be performed mechanically, or by blowing with air or steam, but preferably it is effected by means of the saturated ammonium sulphate solution, which enters at a point near the bottom of the conical-shaped treatment vessel containing the crystals. The rapid stream on entering stirs up the crystals but as the diameter of the vessel increases only the impurities remain suspended. Fig. 1 indicates a saturator A from which crystals are removed to the vessel C by means of steam lift B. A stream of filtered saturated ammonium sulphate enters by pipe d, and is regulated by valve r. The temperature of the liquor throughout the system is maintained at the same temperature as the crystals coming from the saturator, by means of steam coils in the storage tank D and the filter F. The clean crystals are discharged periodically on to the drainer H, the liquor collecting in the sump G from which it is raised to tank D by means of an air lift. An ordinary saturator may also be adapted for the process. Crystals having been deposited, the passage of ammonia is reduced or stopped. A filtered saturated solution of sulphate of ammonium is supplied near the bottom of the saturator and overflows through a launder and passes to the filter as previously described.

FIG. I.




Messrs. Rayner & Co., will obtain printed copies of the published specifications and forward on post free for the official price of 1/- each.

## MEETINGS FOR THE WEEK.

*Monday, January 31, 1921.*

Royal Society of Arts, 8.

*Tuesday, February 1.*

Royal Institution, 3. "The British Soldier since the Restoration—In Peace," by Hon. J. W. Fortescue.
Royal Society of Arts, 4.30.
Röntgen Society, 8.15.

*Wednesday, February 2.*

Royal Society of Arts, 4.30.
Society of Public Analysts, 8. (Annual Meeting). "Extract of Red Squill as a Rat Poison," by F. W. Smith. "Composition of Harrogate Mineral Waters," by W. Lowson.

*Thursday, February 3.*

Royal Society, 4.30. "The field of an electron on Einstein's Theory of Gravitation," by G. B. Jeffery. "A Physical Theory of Stellar Spectra, by M. N. Saha "The ultramicroscopic Structure of Soaps," by W. F. Darke, J. W. McBain, and C. S. Salmon. "Linear Transformations and Functions of positive Type," by J. Mercer.
Royal Institution, 3. "Oceanography—Great Exploring Expeditions," by Prof. W. A. Herdman.
Society of Chemical Industry, 7.30. (At Bristol).
Chemical Society, 8.

*Friday, February 4.*

Royal Institution, 9. "Electrical Expression of Human Emotion," by Augustus D. Waller.
Society of Chemical Industry, 7. (Manchester and Cardiff).

*Saturday, February 5.*

Royal Institution, 3. "The Madrigal—Technique," by Percy C. Buck.

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All communications should be addressed to the MANAGER, CHEMICAL NEWS, 97, SHOE LANE, LONDON, E.C.4.

THE CHEMICAL NEWS.

VOL. CXXII., No. 3173.

## ON DENTAL INCRUSTATIONS AND THE SO-CALLED "GOLD-PLATING" OF SHEEP'S TEETH.

By THOS. STEEL.

FOR many years past there have appeared from time to time, in newspapers and magazines published all over the world, statements as to the occurrence of a metallic incrustation on the teeth of sheep. The incrustation in question is usually found more or less thickly coating the sides of the molar teeth, and, being frequently of a shining, yellowish, metallic appearance, has been popularly attributed to gold supposed to have been derived from particles of that metal scattered about the pastures. So deeply-rooted is the popular belief that the incrustation consists of gold, my friend, Mr. J. H. Campbell, informs me that persons have brought jaws of sheep to the Royal Mint, Sydney, with a view to selling them for the supposed adherent gold. Quite recently, it was most confidently asserted by correspondents in *Nature*, 1917, xcix., 264, 284, 290, 306; 1917, c., p. 106, that the incrustation consisted of iron pyrites, and various fantastic theories were put forward to account for the presence of this substance in such a situation.

In 1905, Prof. Liversidge exhibited at a meeting of the Royal Society of New South Wales part of a sheep's jaw, heavily coated with yellow metallic looking deposit, and read a descriptive note with a qualitative analysis, clearly showing the true nature of the substance to be a deposit derived from the saliva, and that the metallic appearance was due to the refraction of light by the overlapping edges of the thin lamellae of the deposit (*Journ. Roy. Soc., N.S. Wales*, 1905, xxxix., 33; also CHEMICAL NEWS, 1905, xcii., 115; *Journ. Soc. Chem. Ind.*, 1905, xxiv., 1039. Again, in July, 1905, the same gentleman exhibited and explained the deposit at a meeting of the Sydney section of the Society of Chemical Industry. Similar specimens were exhibited by Horan to the New South Wales Naturalists' Club in 1913 (*Australian Naturalist*, 1913, ii., 174, 187).

As will be shown in this paper, the presence of such deposits is by no means confined to the teeth of sheep, but is a common occurrence on those of a very large variety of animals, including man. It is, in fact, a dental calculus analogous to those occurring in the urinary tract.

The earliest account of the true nature of dental incrustations with which I have met, occurs in the *Annals of Philosophy* (Thomson's *Ann. Phil.*, 1814, ii., 380). In the course of a series of articles entitled "General Views of the Composition of Animal Fluids," Berzelius gives a correct explanation of the nature of the deposit from human teeth, and his analysis of a specimen, which will be quoted further on.

In 1834, Dr. G. Bennett ("Wanderings in New South Wales," 1834, i., 294) records having observed a layer of "metallic substance" incrusting the teeth of kangaroos, and correctly diagnosed it as "tartar" precipitated from the saliva. He mentions its occurrence in the ox and sheep, and remarks that on account of its yellow colour it is frequently mistaken for gold. He quotes the analysis by Berzelius mentioned above.

In a paper published in 1879, "On Macrodontism," N. de Miklouho-Maclay (*Proc. Linn. Soc. N.S. Wales*, 1879, iii., 169) described and figured the huge projecting teeth which he observed in natives of the Taui or Admiralty Islands, and refers to a sketch in *Nature*, 1877, xvi., 251, which he describes, however, as a caricature. In a subsequent paper (*Proc. Linn. Soc. N.S. Wales*, 1886, x., 682) he explains that further investigation had shown that he was mistaken in supposing that the projections were due to dental malformation, but that they really consisted of an enormous deposit of "tartar," probably largely due to the habit of these people of chewing betel nut and lime. The deposit could be detached, leaving the teeth quite normal. The late Mr. R. P. Pedley, surgeon-dentist, who examined the deposit, identified it as dental tartar. Unfortunately there is no record of a chemical examination having been made. Miklouho-Maclay proposed the term "odontolithiasis" for this condition.

From the stocks of bones passing through a large bone charcoal factory in Sydney, I have been able to examine the teeth of numerous sheep, and also those of oxen, horses, pigs, etc., and to secure ample material for a complete chemical analysis of the deposit from the teeth of sheep and oxen. From other sources I have obtained sufficient for quantitative analysis from the teeth of a number of animals, including man. By the courtesy of the late Mr. R. Etheridge, specimens from the teeth of animals in the Australian Museum, Sydney, were secured, sufficient in a few cases for full analysis, and in a considerable number of others for qualitative determination. Mr. H. A. Longman, F.L.S., Director of the Queensland Museum, kindly allowed me material from the skeleton of a camel. In all such cases care was taken to insure that the deposit obtained was pure and not contaminated with lime which may have been used in the preparation of skeletons.

Very commonly the taxidermists appear to have carefully cleaned the teeth. My kinsman, Mr. A. Ross Brown, B.D.Sc., L.D.S., of Windsor, Melbourne, and my friend, Mr. J. Darton, surgeon-dentist, Petersham, furnished me with an ample supply from human teeth, secured in the course of their professional practice in the operation of "scaling." Mr. Charles Hedley, Acting Curator of the Australian Museum, kindly gave me facilities, with the aid of Messrs. Thorpe and Troughton, to examine the large collection of skulls in the Museum. To Prof. J. Douglas Stewart, of the Veterinary School, Sydney University, I am indebted for explaining to me details regarding the structure of teeth and giving me other information. To all of these gentlemen I desire to tender my best thanks. Further material was obtained from specimens in my own collection and passing through my hands. In addition to examining the dental deposit, I have, in the cases of the ox and camel, made an analysis of the cement or cementum layer (*crusta petrosa*). In these animals this layer is strongly developed, extending well up on the exposed part of the tooth, and

*Analyses of Dental Incrustations*

| | Man | Sheep | Ox | Camel | Dromedary | Rhinoceros | Babirussa | Cement layer (*Crusta petrosa*) Ox | Camel |
|---|---|---|---|---|---|---|---|---|---|
| Lime (CaO) ... ... ... | 40·75 | 28·00 | 29·38 | 37·75 | 37·00 | 46·13 | 47·50 | 35·69 | 36·21 |
| Magnesia (MgO) ... ... | 0·18 | 4·19 | 3·69 | 0·27 | 0·18 | 0·56 | 0·68 | 1·12 | 0·98 |
| Phosphoric oxide ($P_2O_5$) .. | 34·73 | 26·55 | 28·17 | 29·33 | 29·48 | 7·95 | 7·14 | 26·68 | 26·88 |
| Carbon dioxide ($CO_2$) .. | 1·32 | 1·45 | 1·10 | 2·70 | 2·88 | 22·65 | 41·63 | 2·90 | 1·80 |
| Organic matter* .. ... | 17·23 | 24·65 | 23·90 | 16·20 | 16·82 | 17·48 | 41·63 | 23·54 | 24·74 |
| Water at 110° C. ... ... | 5·38 | 11·03 | 10·30 | 11·65 | 10·40 | 3·85 | 2·63 | 9·35 | 8·66 |
| Sand ... ... ... .. ... | 0·10 | 2·30 | 2·00 | 0·60 | 0·30 | 0·55 | 0·39 | nil | nil |
| Undetermined and loss ... | 0·31 | 1·83 | 1·46 | 1·50 | 2·94 | 0·83 | 0·03 | 0·72 | 0·73 |
| | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |
| *Containing nitrogen ... | 1·20 | 1·48 | | | | 0·74 | | | |
| Sp. Gr. ... ... ... ... | 2·317 | 2·025 | | | | | | 2·112 | |

can be readily separated. The incrustation could, in most cases, be easily flaked off from either the cement or the enamel and the surface beneath was always quite sound.

The figures following give the results. The samples were ground, and air-dried at ordinary temperature.

Miklouho-Maclay mentions that specimens of teeth similarly encrusted to those which he describes were forwarded by F. A. de Roepstorff from the Nicobar Islands to Professor Virchow, Berlin (*Verh. Berlin. Ges. Anthrop.*, June, 1881, p. 219) The deposit from these was analysed by Salkowski, and the results published by Virchow, the following being the figures :—

| | |
|---|---|
| Water ... ... ... ... ... | 5·95 |
| Organic matter ... .. ... ... | 9·10 |
| Silica and iron oxide ... ... | 0·87 |
| Iron phosphate ...... ... ... | 2·26 |
| Lime ... ... ... ... ... ... | 45·24 |
| Magnesia ... ... ... ... ... | 0·68 |
| Phosphoric oxide ... ... ... | 30·73 |
| Carbon dioxide ... ... ... ... | 4·87 |
| | 99·70 |

This shows more lime and carbon dioxide and considerably less organic matter than I found in the normal incrustation from human teeth. Probably this is a result of the addition of carbonate of lime from the lime-betelnut habit, but the high phosphoric acid shows that essentially the deposit has been derived from the saliva. The presence of so much iron phosphate is peculiar, and I am unable to explain it. I found no appreciable iron in any of my samples.

The analysis by Berzelius mentioned above, is thus stated :—

| | |
|---|---|
| Earthy phosphates ... ... ... | 79·0 |
| Mucus ... ...... ... ... ... | 12·5 |
| Peculiar salivary matter ... ... | 1·0 |
| Animal matter soluble in muriatic acid ... ... ... ... | 7·5 |
| | 100 |

There is no mention of water. It is probable that Berzelius merely ignited and took the ash as "earthy phosphates," and the organic substances include water. For a rough comparison it will suffice to consider the "phosphates as being tribasic phosphate of lime and to lump together the organic substances. This would give :—

| | |
|---|---|
| Lime ... ... ... ... ... ... | 43·0 |
| Phosphoric oxide ... ... ... | 36·0 |
| Organic matter and water ... | 21·0 |
| | 100·0 |

These figures agree very well with my analysis of the human product. In my examination I found the total loss on ignition, including water and carbon dioxide, was 24 per cent, and the ash 76 per cent.

In my analysis, in every case the sand was in the form of mechanically embedded grains. It will be noticed that the incrustations from the Rhinoceros and Babirussa (a pig-like animal from N. Celebes) differ from the others in containing but little phosphoric acid and a considerable proportion of calcic carbonate. In both of these the scale, when detached, was in appearance much like that from the sheep and ox, being in clean shining flakes. In man it is chalky-looking and has not got the metallic, or more commonly, nacreous look of that from the sheep. The similarity in composition between most of the incrustations and that of the cement layers of ox and camel is striking. Ordinary mammalian bone has also a very similar composition ("Watt's Dict. Chem.," 1879, vi., 1st Supp., 357).

In making the analyses, care was taken in separating lime and magnesia, by double precipitation of the lime in the cold to avoid co-precipitation of magnesia. The proportions of lime and phosphoric acid present are such as to indicate that the phosphate of lime does not exist entirely as the tribasic ($Ca_3P_2O_8$), but that a variable amount of the tribasic ($Ca_4P_2O_9$) is also present. I have found this to be a usual condition in many natural phosphates such as those from Ocean Island.

Bearing in mind the analogy between these dental salivary incrustations and urinary calculi, a careful examination was made of those from man, sheep, and ox, for oxalic and uric acids, but with entirely negative results.

I have examined the deposit from a large variety of animals in addition to those already mentioned, using micro-chemical methods when the amount available was minute, and in every case have found it to be of substantially the same nature. The quantity present varies from a mere trace of brown film, to a heavy incrustation packed round the crowns of the teeth and forming a continuous coating along the sides as much as a quarter-of-an-inch in thickness. It is heaviest in herbivorous animals and in man. The teeth of the carnivorae and rodents are usually very clean; this is well seen in dogs, cats, mice, and rats, though all of these, particularly when old, and also rabbits, frequently have a thin brown film even on the incisors. Some individuals are more predisposed to dental incrustation than others. This is well-known in man, and I have noticed it

in sheep, and other animals. The teeth of snakes, lizards, and fish, in so far as I have noticed, appear to be always quite free from deposit.

I do not think that the nature of the pasture, as has sometimes been asserted, has anything particular to do with the abundance or otherwise of deposit on sheep's teeth, but that it is purely a physiological idiosyncrasy. Sheep and oxen very commonly have the teeth coated with a uniform thin, dead black film, but this does not differ in composition from the thicker deposit. The common pig has very clean teeth. I have examined many hundreds of pigs' jaws, and have never noticed more than traces of a brown film.

Extended observation has satisfied me that the incrustation, in greater or less degree, is common to all mammals, and also to a number of other animals, in every case being of the same general character. I have found it, for instance, in the crocodile (*C. porosus*) Queensland, killer whales (*Orca gladiator*), and in one individual or another of practically every mammalian species examined. It will suffice to give the names of a few as indicating the scope of the investigation: tapir, eland, American bison, hippopotamus, various bears, dog, cat, rat, mouse. Examination of the skulls of marsupials in the Australian Museum collection and elsewhere disclosed numerous examples: *Macropus major*, quite as heavy as that of the sheep, *M. giganteus*, *M. rufus*, *Phascolarctus cinereus*, *Phascolomys mitchelli*, *Dasyure*, and many others. The original observations of Dr. Bennett are thus completely confirmed. Fossil marsupial teeth from Wellington Caves, New South Wales, in the Australian Museum, still have adhering brown patches which I take to be the same deposit. Wherever the teeth of animals were noticed to have a yellow or brownish tint as in aged rats, minute examination showed this to be due to the same cause.

In response to queries from me, Mr. Brown has supplied me with the following very interesting notes: "Tartar forms on artificial *plates*, especially lower plates, quite as readily as on the natural teeth; it is an everyday occurrence to see that. It is deposited along the lower portion of the lingual side of the *plate*, and dentists are continually asked by patients what it is and how to remove it. I do not remember seeing teeth forming part of a bridge with tartar deposited on them, but frequently find that the gum having slightly receded after the bridge has been fixed, a slight deposit is to be seen round the gingival margin of the natural roots to which the bridge is attached. Porcelain crowns (pivots) and gold crowns or caps remain free from deposit. I once had to remove from an elderly woman's mouth a little lower plate having three teeth on it, and there was such an accumulation of tartar all about the whole structure and the remaining teeth that two of the latter were extracted in the removal of the plate; these, however, were loose from pyorrhoea. In this case case the tartar had certainly encroached to some extent on the artificial teeth. The patient informed me that she had not removed the denture since the dentist put it in place many years before This case was an exceptional one, and as I have mentioned, I do not remember seeing deposit on artificial teeth at any other time."

I think it is probable that the nature of the surface of porcelain teeth and gold crowns inhibits the adhesion of deposit. In the case of the urinary tract, it is well known that any solid foreign body, such as a piece of broken catheter, soon becomes coated with phosphate, and that a little blood clot or even bacteria may form the nucleus of a urinary calculus.—*Proceedings of the Linnean Society of New South Wales*, August 25, 1920.

## THE SUBSTANCES DISSOLVED IN RAIN AND SNOW.

By WILLIAM A. MOORE and GLEN BROWNING.

THE precipitations in Mount Vernon, Iowa, from May 31 to August 13, 1920, were studied in the chemical laboratories of Cornell College. Mount Vernon is a village of about 2000 population, situated 18 miles from the nearest manufacturing centre. The rain was caught in two porcelain receptacles, about 20in. in diameter, in an open space away from trees and as far as possible from chimneys.

There were 21 precipitations during the time, and a total rainfall of 6·13 inches. The precipitations were tested for nitrogen in nitrates, nitrites, free and albuminoid ammonia. The water was also tested for phosphates, and to our surprise they were frequently found to show a trace. Sulphates were found in a number of the samples. Chlorides were found to be absent in the first two or three precipitations, and so we discontinued the tests in the later rainfalls.

We expected more than the usual amount of nitrogen in the precipitations during thunder storms, but such did not prove to be the case. For the first time in the history of these investigations carbon dioxide was sometimes detected.

When there was a small amount of precipitation, the analysis showed a relatively large amount of all the various substances. We also noticed when the wind was blowing from the manufacturing centre previous to the rainfall, there were carbon dioxide and sulphates almost invariably present.

On one occasion there were two precipitations in the same day. Both were analysed and while the first contained 0·001 parts nitrites and 0·3 parts nitrates per million, the second contained only 0·0009 parts nitrites and 0·005 parts nitrates. This decrease was always in evidence after a rain following one on the previous day.

The precipitation of the afternoon of July 4 which was 1in., contained a large amount of all the substances usually found. The ammonias were 0·6, nitrates 0·35, carbon dioxide 0·6 per million; while the average for the summer months was ammonias 0·28, nitrates 0·35, carbon dioxide, 0·23.

The amount of nitrogen as nitrites and nitrates which fell during this period of three months was 0·76lb. per acre.

In previous papers we have suggested the spray from the Atlantic Ocean borne by the winds across the country as the source of the sodium chloride in the atmosphere, and precipitations of both rain and snow. Dr. Charles T. Brooks, of Washington, D.C., editor of the *Monthly Weather Review*, kindly called our attention to dust storms and muddy rains from the arid regions of the

outh-western part of the United States as a posible source of the sodium chloride in the atmoshere. He cites especially such a storm of March, 918, described by A. N. Winchell and E. R. Miller in the *Monthly Weather Review* of November, 1918. During the storm, material was arried several hundred miles, depositing dust at Dubuque, Iowa, and various other places. Phyical and microscopic examinations of the dust collected at different localities shows that it is chiefly quartz and feldspar with considerable imonite and haematite. The observers menioned also concluded that "the dust is the product of physical disintegration and not of chemical decomposition." There is no indication that any of he observers detected sodium chloride; yet it night have been present in small quantities, and not have responded to the tests to which the deposits were subjected.

Cornell College, Mount Vernon, Iowa.
January 1, 1921.

## THE CHEMISTRY AND CRYSTALLOGRAPHY OF SOME FLUORIDES OF COBALT, NICKEL, MANGANESE AND COPPER.*

By FLOYD H. EDMINSTER and HERMON C. COOPER.

(Concluded from p. 45.)

*Calculations.*—In the computation of the formulas for the fluorides, use was made of the analyses on crystals which were taken from the solution, washed, dried, and analysed immediately. The average of these analyses was used.

In the case of fluorine results from the precipitation by calcium chloride alone were discarded, as they had been proven to be inaccurate. The results used are the average of the fluorine determinations by titration and by precipitation by calcium chloride in the presence of calcium oxalate.

For the metal the calculations in the case of cobalt, nickel, and copper are the average of results obtained from the anhydrous sulphate and by electrolysis, with emphasis upon the latter, since in this method the sources of error are reduced to a minimum. For manganese metal the calculations are based upon the weight found in the anhydrous sulphate and in the pyrophosphate.

For the water use was made of the percentage difference.

In some cases only selected determinations were utilised for the calculations. The selection is given in the last column of the following tables. A great many more determinations were made than are recorded in the preceding tables, in order to familiarise ourselves with the possible sources of error.

### *Formulas.*

#### *Cobalt Fluoride.*

Co = 19·40 ÷ 58·97 = 0·3291 = 1·000 All determinations.
F = 43·14 ÷ 19·00 = 2·2705 = 6·899. Nos. 90, 130, 131.
$H_2O$ = 36·06 ÷ 18·00 = 2·0033 = 6·087. By difference.
H = 1·6.
The formula is $CoF_2.5HF.6H_2O$.

*A more detailed account of this work was submitted to the Faculty of the Graduate School of Syracuse University by Floyd H. Edminster in May, 1918, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

#### *Nickel Fluoride.*

Ni = 19·50 ÷ 58·68 = 0·3323 = 1·0000. All determinations.
F = 43·32 ÷ 19·00 = 2·2800 = 6·8610 Nos. 89, 96, 131.
$H_2O$ = 35·58 ÷ 18·00 = 1·9767 = 5·9485. By difference.
H = 1·6.
The formula is $NiF_2.5HF.6H_2O$.

#### *Manganese Fluoride.*

Mn = 18·09 ÷ 55·00 = 0·3283 = 1·000. No. 76.
F = 43·02 ÷ 19·00 = 2·2640 = 6·889. No. 76.
$H_2O$ = 35·58 ÷ 18·00 = 2·0772 = 6·327.
H = 1·5.
The formula is $MnF_2.5HF.6H_2O$.

#### *Copper Fluoride.*

(Crystals by recrystallisation from water).
Cu = 20·09 ÷ 63·57 = 0·316 = 1·000. All determinations.
F = 42·70 ÷ 19·00 = 2·250 = 7·100. All determinations.
$H_2O$ = 35·61 ÷ 18·00 = 1·978 = 6·260. By difference.
H = 1·6.
The formula is $CuF_2.5HF.6H_2O$.

#### *Copper Fluoride.*

(Small crystals and crust deposited slowly from original mixture).
Cu = 45·82 ÷ 63·57 = 0·747 = 1·000.
F = 28·13 ÷ 19·00 = 1·480 = 2·036.
$H_2O$ = 26·05 ÷ 18·00 = 1·440 = 2·000.
The formula is $CuF_2.2H_2O$.

We append here the results of a few determinations and calculations on the crust or powder formed in the preparation of crystals of cobalt and nickel fluorides.

#### *Cobalt Fluoride—Crystalline Crust.*

| Reference No. | Fluorine Per cent. | Metal | Ratio. |
|---|---|---|---|
| 84 | 25·09 | 33·99 | 1·0 : 2·29 |
| | | | Powder. |
| 104 | 24·42(a) | 35·19 | 1·0 : 2·154 |

(a) Average of two determinations on the same material; fluorine also determined on same powder.

#### *Nickel Fluoride—Powder.*

| | | | |
|---|---|---|---|
| 100 | Not det'd. | 34·51 | |
| 101 | 25·46 | 34·66 | 1·0 : 2·26(b) |

(b) Made by boiling the crust.

The results approximate the neutral salt formula and correspond to the result for the copper fluoride crust. We do not, however, feel warranted in assigning formulas.

### *Crystallography.*

From the second recrystallisation in the open air crystals were obtained in ample quantity for crystallographic investigation and analysis. Some of them were as large as 20×8 mm. Measurements were made with a Goldschmidt reflecting goniometer. In general, the specimens were found to be extensively etched because of their high solubility. The etching caused so much dispersion of light that the reflected image was not as sharp as was desirable; therefore the readings were only reliable to about 30 seconds.

*Cobalt Fluoride,* $CoF_2.5HF.6H_2O$, Rhombohedral.—The cobalt fluoride is orange-red; equivalent wave length 610 $\mu\mu$ for a plate 2 mm. thick. (A considerable number of these observations were made or confirmed by H. E. Merwin, of the Geophysical Laboratory, to whom we are accordingly

greatly indebted). The crystals are flattened hexagonal prisms capped by two rhombohedrons of the opposite order to the prisms. The average angle between the prism faces $m : m'$ is 60° 0'. For the rhombohedrons the angles from the base are 30° 59' and 50° 6', both within ± 8'. From the measurements $c$ = 1·039; $c \wedge r$ (10$\bar{1}$1) = 50° 9' and $c \wedge e$ (01$\bar{1}$2) = 30° 55'. Distinct prismatic cleavage was observed. Optically the crystals are uniaxial postive with approximate refractive indices measured by immersion: $\omega$ = 1·38(5), = 1·39(7). Extinction is parallel. The sp. gr. by the Jolly balance, using alcohol as immersion liquid, is 2·0445.

It does not seem worth while to make drawings of the crystals because of their distortion, which was probably due to their growing attached by one side to the dish.

*Nickel Fluoride,* $NiF_2.5HF.6H_2O$, Rhombohedral.—The nickel fluoride is blue-green; equivalent wave-length 510 $\mu\mu$ for a plate 2 mm. thick; non-pleochroic, with habit, cleavage and general optical properties like cobalt fluoride. Measurements of the rhombohedrons gave the same angles as the cobalt salt. Refractive indices measured on a small prism gave the following results for the mercury lines; the other values are interpolated:

| | $\omega$ | $\epsilon$ |
|---|---|---|
| Hg 436 | 1·398 | 1·413 |
| F | 1·395 | 1·410 |
| Hg 578 | 1·392 | 1·408 |
| D | 1·392— | 1·408— |
| C | 1·390 | 1·406 |

Sp. gr. in alcohol, 2·0006.

*Manganese Fluoride,* $MnF_2.5HF.6H_2O$.—The manganese fluoride is light red with habit and general optical properties like those of cobalt fluoride. The average angle between the prism faces $m : m$ is 60° 8'. The pyramid faces were so poorly developed that it was impossible to measure them. Sp. gr. in alcohol, 1·921.

*Copper Fluoride,* $CuF_2.5HF.6H_2O$, Monoclinic.—The copper fluoride is blue-green-blue, equivalent wave-length 490 $\mu\mu$ for a plate 2 mm. thick, and is distinctly pleochroic. The crystals were not perfect enough to determine by form. Microscopically they apparently show three cleavages, to one of which they extinguish parallel. This cleavage seems to be parallel to a set of faces. The extinction observed against another apparent cleavage is very oblique. A few elongated rough crystals and cleavage fragments were elongated in the direction of $\alpha'$. Good biaxial interference figures showed —2E = 48° ± 2°, with no observable axial dispersion. The refractive indices were measured carefully under the microscope by immersion as follows: $\alpha$ = 1·395, $\beta$ = 1·440, $\gamma$ = 1·444. Therefore, —2V = 32°. $\alpha$ is least absorbed.

The evidence of monoclinic symmetry is thus almost conclusive. The examination of the optical properties was rendered very difficult by the rapid loss of crystal hydrate water. Sp. gr. in alcohol, 2·4055.

The crystals of the normal fluoride, $CuF_2.2H_2O$, were too small to measure. Recrystallisation yielded the acid fluoride.

*Isomorphism.*—The chemical and optical examination thus showed that the acid fluorides of cobalt, nickel, and manganese are isomorphous, while the similarly prepared copper fluoride, of the same chemical formula, has a different crystal form. The first three are rhombohedral, forming flattened hexagonal prisms, capped by two rhombohedra of the opposite order to the prisms. All three showed prismatic cleavage, are uniaxial positive, and give parallel extinction. The refractive indices of the cobalt and nickel fluorides differ by less than 1 per cent. The indices of the manganese fluoride were not measured.

*Summary.*

The fluorides of cobalt, nickel, manganese, and copper can be prepared by dissolving either the hydroxide or the carbonate of the metal in hydrofluoric acid, the same product being obtained, whichever is used. In all cases a crust-like product was obtained as the result of evaporating the original solution. From the water extract, slightly acidulated with hydrofluoric acid, crystals of the acid fluorides were formed and analyses and measurements of these crystals were made.

The formulas of all four fluorides are of the same acid fluoride type: $MF_2.5HF.6H_2O$. It was a surprise to obtain the acid fluoride by recrystallisation from water, it being considered more likely that a basic salt would be obtained under these circumstances.

The acid fluorides are not permanent in the air, but decompose, losing hydrogen fluoride, and in the case of copper losing water also, so that the crystals used for analyses must be carefully selected and preserved. Investigation of the rate of loss of hydrogen fluoride was not undertaken, but our analyses were made with crystals soon after being taken from the solution and in our opinion the results are the most reliable obtainable.

The formation of a hydrated, non-crystalline crust is distinct from that of the hydrated acid fluoride crystals. In this crust the ratio of metal to fluorine, for the cases of cobalt and nickel, was found to be, roughly, one to two, with varying water content. This crust differs from the crystals in solubility and form, as well as in composition. We have arrived at the conclusion that the crust described by Berzelius as containing two molecules of water, the crust later described by Clarke as containing three molecules of water, and the crust and powder obtained by use are the same, the water content being variable and the crystal form undeveloped. All were obtained in the same manner.

The acid fluorides of cobalt, nickel, and manganese give rhombohedral crystals, with prismatic cleavage, parallel extinction and uniaxial positive character. Since they have the same type of chemical formula, the same crystal form and the same habit, cleavage and general optical properties, we consider that they constitute an isomorphous series.

The acid fluoride of copper has the same type of formula, but differs crystallographically.

From the original preparation of copper fluoride small crystals of the normal fluoride, $CuF_2.2H_2O$, were obtained, which were not good enough for measurement and which reverted unexpectedly to the acid fluoride on recrystallisation from water.

The experimental work upon which this article is based was completed in May, 1918.

## ON FERRAZITE? A NEW ASSOCIATE OF THE DIAMOND.

By T. H. LEE and LUIZ FLORES DE MORAES.

Among the voluminous researches of the late Eugen Hussak, some of the most interesting are his patient investigations of the dense minerals found in diamond-washing, which extended over a number of years.

Apart from the great number of minerals studied and determined by him and made known to the scientific world by the publication of his posthumous work "Os satellites do Diamante," edited by our colleague Dr. Jorge Belmiro de Araujo Ferraz, considerable and valuable material exists in the Hussak mineral collection, acquired and conserved by the Brazilian Geological Service, in which our colleague encountered and handed to us for analysis a number of "favas" with Hussak's own label "Pb-Al hydrophost. D.-3·095.Neu! (*Favas*: English equivalent "Beans." This name is applied to certain dense rounded flattish pebbles found with the dense residues from gravel in the diamond-washers batéas).

From the results of a preliminary analysis it appeared that, in addition to lead, barium was also present, which led us to carry out a complete analysis, leading to the following results:—

| | |
|---|---|
| Combined water | 14·20 |
| Lead oxide | 45·63 |
| Barium oxide | 8·87 |
| Lime | traces |
| Alumina | 3·48 |
| Phosphoric Anhydride | 26·24 |
| Silica | 2·44 |
| | 100·86 |

Considering the silica to be present as kaolinite, and the excess of alumina over and above that required by the silica to be present as wavellite, the composition of the "favas" should be represented as follows:—

| | New Mineral | Kaolinite | Wavellite |
|---|---|---|---|
| Combined water | 12·48 | 0·71 | 1·01 |
| Lead oxide | 45·63 | — | — |
| Barium oxide | 8·87 | — | — |
| Alumina | — | 2·05 | 1·43 |
| Phosphoric anhydride | 24·92 | — | 1·32 |
| Silica | — | 2·44 | — |

Calculating anew the composition of the new mineral on a centesimal basis, we have:—

| | | Molecular ratios. |
|---|---|---|
| Combined water | 13·58 | 0·7544 |
| Lead oxide | 49·65 | 0·2227 |
| Barium oxide | 9·65 | 0·0631 |
| Phosphoric anhydride | 27·12 | 0·1910 |
| | 100·00 | |

Recalculating these molecular ratios on a basis of $P_2O_5$ equal to 2, we have:—

| | |
|---|---|
| Combined water | 7·900 |
| Lead and barium oxides | 2·993 |
| Phosphoric anhydride | 2·000 |

or 3 $(Ba,Pb)O.2P_2O_5.8H_2O$.

The density of the "favas" varies between 3·0 and 3·3. The colour is a dark yellowish-white, resembling that of old ivory. The specimens are discoid in shape, and thin sections show under the microscope a granular structure suggesting that resulting from the evaporation of a colloid substance.

Dana's "System of Mineralogy," 6th ed. with Supplements I. and II., mentions no such mineral, although it includes all Damour's results, so that we feel justified in claiming novelty for the mineral, and suggest for it the name of *Ferrazite*, in just recognition of Ferraz's valuable work in editing Hussak's posthumous work, and in classifying and rendering available the precious mineral collection left by him.—*American Journal of Science*, xlviii., p. 353.

## THE CRYSTAL STRUCTURE OF ICE.

By D. M. DENNISON.

*Synopsis.*

*Crystal Structure of Ice as Determined from X-ray Pattern.*—A small sample of ice composed of minute crystals, gave by Hull's method a pattern of 12 clearly-defined lines whose positions indicate that the lattice of an ice crystal corresponds to a hexagonal close-packed arrangement of molecules, consisting of two sets of interpenetrating triangular prisms with sides 4·52 A and height 7·32 A. Since for close-packed spheres the axial ratio should be 1·633 instead of 1·62, the ice molecules act like spheres which have become flattened by 0·8 per cent in the direction of the hexagonal axis. This lattice is practically the same as that found for magnesium, but the differences in relative intensity between the lines of the two X-ray patterns suggest that ice molecules and magnesium atoms must differ considerably in shape.

*Molecular Formula for Ice.*—From the density of ice and the dimensions of the lattice it follows that the formula for an ice molecule is $(H_2O)_2$ or $H_4O_2$.

X-ray photographs of ice were made in the same manner as the crystal powder photographs described by W. A. Hull (*Phys. Rev.*, Jan. 1917, ix., 85). A small quantity of distilled water was enclosed in a thin-walled capillary tube of lime glass. The tube was then plunged quickly into liquid air, freezing the water with such rapidity that only very minute crystals were formed. The tube was then kept at liquid air temperature in a specially constructed Dewar flask. The sample was rotated continuously during the 10-hour exposure to the X-rays from the molybdenum target of a water-cooled Coolidge tube which was running at 32,000 volts, 25 milliamperes direct current. The photographic film was bent in a semicircular arc of radius 19·8 cm. The tube of ice was placed in the axis of this arc. A good photograph was obtained which contained 12 lines, the data from which are recorded in the table.

The first column gives the angular deviation of each line, the second gives the intensities, which were only roughly estimated, and the third gives the intensities of the corresponding magnesium lines as estimated by Dr. Hull (*Pro. Nat. Acad. Sci.*, July, 1917, iii., 470). The fourth column gives the observed plane spacings, while the fifth gives the theoretical plane spacings which would correspond to a close-packed hexagonal lattice,

consisting of two sets of interpenetrating triangular prisms, the sides of whose bases are each 4.52 Ångstroms and whose height is 7·32 Ångstroms. The observed and theoretical spacings agree within the limit of experimental error.

| Angular Deviation of Line $2\theta$ (Degrees). | Intensity of Line (Estimated). | Intensity of Magnesium Line for Comparison. | Spacing of Planes in Ångstroms Obs. | Spacing of Planes in Ångstroms Cal. | Indices of Form | No. of Cooperating Planes |
|---|---|---|---|---|---|---|
| 10·44 | 1 | 4·7 | 3·92 | 3·915 | 1010 | 3 |
| 11·16 | 10 | — | 3 67 | 3·671 | 0001 | 1 |
| 11·88 | 2 | 10·0 | 3·44 | 3·453 | 1011 | 6 |
| 15·30 | 1·5 | 3·3 | 2·68 | 2·675 | 1012 | 6 |
| 18·12 | 1 | 4·7 | 2·26 | 2·260 | 1120 | 3 |
| 19·86 | 5 | 4·0 | 2·065 | 2·065 | 1013 | 6 |
| 21·38 | .1 | 4·0 | 1·92 | 1·925 | 1122 | 6 |
| 27·16 | 1 5 | 1·0 | 1·516 | 1·528 | 2023 | 6 |
| 30·20 | 2 | 1·3 | 1·368 | 1·372 | 1015 | 6 |
| | | | 1·368 | 1·372 | 1232 | 12 |
| 31·76 | 0·25 | 0·2 | 1·30 | 1·305 | 1010 | 3 |
| 33·08 | 0·25 | 1·0 | 1·25 | 1·268 | 1233 | 12 |
| 35·54 | 0·5 | 0·3 | 1·167 | 1·165 | 2025 | 6 |

The above values give an axial ratio of 1·62 in good agreement with the crystallographer's value of 1·617 (Gmelin Kraut, "Handbuch der Anorganischen Chemie," Heidelberg, 1907, i., 1, p. 107). An hexagonal lattice of close-packed spheres has an axial ratio of 1·633. The data from the photograph seem to indicate that 1·62 is a more probable value than 1·633 for the structure of ice. This ratio and the dimensions of the elementary prism were determined by means of a set of graphs, made by Dr. Hull and Dr. Davey, which is to be published shortly.

Estimating $p$ the density of ice at liquid air temperature as $p=0·944$, the number $N$ of molecules of $H_2O$ per cubic centimetre may be calculated.

$$N = \frac{p(6·023) \times 10^{23}}{18} = 3·154 \times 10^{22}.$$

The volume $V$ of the elementary prism may also be found, knowing that $a$ the base and $h$ the height of the prism are 4·52 A. and 7·32 A. respectively.

$$V = \frac{\sqrt{3}a^2h}{4} = 0·6478 \times 10^{-22}\text{.c.c.}$$

The number $n$ of $H_2O$ molecules per unit prism is then equal to the product $VN$.

$$n = VN = 2·04.$$

Ice belongs then very nearly to one of the two alternate arrangements which inelastic uniform spheres may assume if packed as closely as possible. This is the same form that magnesium atoms take. If the molecules of ice and the atoms of magnesium were identical in arrangement and form, not only would the plane spacings be proportional but also the intensities of the lines would be similar. From columns two and three of the table it may be seen that the intensities are not proportional. With increased knowledge of crystal structure these data may furnish information regarding the shape of the molecule of water. With the hexagonal close-packed type of lattice each prism contains on the average one molecule. The result calculated above indicates that in ice crystals the molecules of water are of the form $(H_2O)_2$ or $H_4O_2$.—*Physical Review* (*U.S.A.*), January, 1921.

## THE LUMINESCENCE OF SAMARIUM.

By HORACE L. HOWES New Hampshire State College.

THE rare earth elements, in composition with lime or other diluents have been made to phosphoresce by Sir William Crookes (Crookes, *Comptes Rendus*, 1879, lxxxviii., 283), Leecoq de Boisbaudran (Leecoq de Boisbaudran, *Comptes Rendus*, 1885, ci., 552), Urbain (Urbain, *Annales des Chimie et de Physique*, 1909, ser. 8, xviii , 222), and others. The most favoured mode of excitation is by the cathode rays. The long controversy between Urbain and Crookes over the phosphorescent spectra of the rare earths has resulted in the control of those exacting chemical processes whereby the rare earths can be prepared in definite grades of purity. Such beautiful analyses have been made that the physicist is now able to begin his study of the rare earths with an exact knowledge of the composition. The method of making samples for luminescence (using the term "luminescence" to include the older terms "phosphorescence," as well as "fluorescence") can be varied systematically, the heat treatment well controlled, and the variation of the spectra, if present, noted. As has always been found true, heat treatment is necessary to render the specimen in a luminescent condition. The molecular aggregates are no doubt so changed by the heat treatment that luminescent centres are produced in highly localised positions scattered through the general structure.

One of the chief reasons why the rare earths in solid solution offer an excellent field for attacking the problem of luminescent radiation is because of the highly resolved bands which constitute the luminescence spectrum. Hitherto, with the exception of such solids as the uranyl compounds and the ruby and such gases as iodine, sodium, mercury, sulphur, &c., studies have been made with substances, which, although brilliant, exhibit only broad bands. The difficulties in the path when analysis of such very broad bands is attempted are considerable because of the extensive overlapping of the components, but the rare earth compounds present—like the uranyl compounds where very narrow bands are viewed against a dark background—a very convenient field (Nichols and Howes, "The Fluorescence of the Uranyl Salts,"*Publications of the Carnegie Institute of Washington*, No. 198). The present work on samarium must be considered a prelude to a rather complete analysis of rare earth luminescence.

The present problem was the outcome of earlier work done in collaboration with Prof. E. L. Nichols and the investigation was made possible by a grant from the Rumford Fund. The specimens of samarium oxide were obtained from Prof. C. James, of New Hampshire State College, and the solid solutions were prepared by Dr. D. T. Wilber, of Cornell University. The samarium oxide was weighed and dissolved in hydrochloric acid and diluted to 1/100. This solution was added to pure calcium carbonate which had previously been tested for non-luminescence in a proportion which gave one atom of rare earth to 125 atoms of calcium. The mixture was evaporated to dryness with stirring. The heat treatment was carried on in the following manner: limited portions were placed in uncovered glazed crucibles and treated at several temperatures between 200°

and 1200° C. in an electrical resistance furnace. The duration of heat treatment at one temperature was also varied between one and three hours. It was found that it was necessary to heat to a critical temperature of approximately 600° C., to render the luminescence sufficiently bright for spectrum analysis when the specimen was subsequently cooled to +20° C. and excited by the cathode rays. The 200° C. specimens gave no luminescence at all and the 400° C. specimens exhibited but few regions of luminescence. As regards the duration of heat treatment, one hour served as well as three hours—probably because only thin layers were treated. About twenty specimens from the same stock were thus heat treated, and finally one specimen was heated five minutes in the core of an arc carbon. Although no quantitative measurements of intensity were taken it was observed that specimens previously heated to 1200° C., or above that temperature, were the most brilliant under cathode rays at +20° C.

The luminescence spectrum consists of more than thirty bands of varying intensities, which plotted to a frequency scale can be resolved into several series: *a, b, c, d, e, f, g, h, i*, of constant frequency intervals. The intervals, although constant for given series, vary slightly from one series to another; series *a* for example of 110 units interval, series *b* of 108 units interval. In Table I. will be found the wave-length and reciprocal of wave-length of each band together with the relative intensity and series letter. The bands not previously discovered are marked, but the object of the present investigation was to study the conditions under which the spectrum is produced and to analyse it—rather than to discover new bands. The times required for one exposure averaged approximately ten minutes.

TABLE I.

*Luminescence Bands of Samarium Oxide in Calcium Oxide.*

| Nature. | λ. | 1/λ | Series. |
|---|---|---|---|
| v.d. ... ... | 6801 | 1470 | *c* |
| d. ... ... | 6734 | 1485 | *d* |
| v.v.d. ... | 6643* | 1505 | *e* |
| d. .. ... | 6600 | 1515 | *a* |
| d. br. .. ... | 6536 | 1530 | *f* |
| d ... .. | 6470 | 1546 | *b* |
| d. Vag. ... | 6405 | 1561 | *h* |
| d. br. ... ... | 6329 | 1580 | *c* |
| m. br. ... ... | 6270 | 1595 | *d* |
| m. Va. ... ... | 6183* | 1617 | *e* |
| V. str. ... | 6146 | 1627 | *a* |
| v.d.n. ... | 6140* | 1629 | *a'* |
| v.d. .. ... | 6103 | 1639 | *f* |
| v.str. ... | 6050 | 1653 | *b* |
| v.v.d.n. ... | 5990* | 1669 | *h* |
| m .. ... | 5940 | 1684 | *c* |
| v.d.v.n. ... | 5898* | 1695 | *g* |
| m. b. ... ... | 5868 | 1705 | *d* |
| m ... ... | 5793 | 1726 | *e* |
| v. str. ... ... | 5757 | 1737 | *a* |
| v.v.d.n. ... | 5721 | 1748 | *f* |
| v. str. ... ... | 5675 | 1762 | *b* |
| d. ... ... | 5653* | 1769 | *i* |
| v.d. ... ... | 5621* | 1779 | *h* |
| d.Vag. ... | 5581* | 1792 | *c* |
| m ... ... | 5553 | 1801 | *g* |
| v.d.n. ... | 5520* | 1812 | *d* |
| n. ... ... | 5481 | 1824 | — |
| v.d.n. ... | 5451* | 1835 | *e* |
| v.d.n. .. | 5416* | 1846 | *a* |
| v.d.br. .. | 5387* | 1856 | *f* |
| v.d.br. ... | 5328* | 1877 | *i* |

* Wave-lengths of bands hitherto undiscovered.

The most startling behaviour of the samarium oxide rests in the fact that *no shift in the positions of the bands could be measured, whether the specimen was heat-treated at* 600° C. *or* 3000° C. This remarkable stability is *not* generally associated with a luminescent substance, and hence is of great importance. It may be due in part to the greater than ordinary purity of the materials employed as well as to consistency in the conditions of excitation, exposure, &c.

The specimens must be kept in a desiccator or sealed in glass since both the samarium and calcium oxides upon taking water from the air become non-luminescent as a compound. The specimen was mounted on an aluminium shelf which tended to keep the temperature from rising much above room temperature by conducting the heat due to impact to a hollow aluminium cylinder of large area. That this precaution served the purpose of maintaining the temperature of the very thin lamina of the specimen near room temperature was observed in a unique manner. After an exposure it was observed that a small portion of the cathode ray bundle did not strike the specimen but passed on to excite the luminescence particles of the specimen which had fallen to the bottom of the glass tube. When the cathode stream was stopped the particles on the glass surface exhibited brilliant thermo-luminescence due to heating by the cathode rays while the sample on the aluminium shelf showed no thermo-luminescence.

Subsequently it was found that the temperature required for thermo-luminescence was approximately 200° C.

*Summary.*

1. The spectrum of the cathode-ray luminescence of samarium oxide in calcium oxide is unchanged by heat treatment at several temperatures ranging from 600° to 3000° C.

2. The spectrum consists of eight short series of constant frequency intervals.—*Physical Review (U.S.A.)*, January, 1921.

## PROCEEDINGS OF SOCIETIES.

### MINERALOGICAL SOCIETY.

*January* 18, 1921.

"*The Olivine Group.*" By A. F. HALLIMOND.

Since the discussion of the densities by Thaddéef in 1896, and of the optical constants by Backlund in 1909, numerous additions have been made to the published data. These have been collected, and the most probable values for the pure compounds obtained. The molecular volume of monticellite is slightly greater than the mean between forsterite and $\gamma$-$Ca_2SiO_4$. For the complex mixtures the density and mean refractive index yield additive relationships, but the birefringence and axial ratios follow no additive law. The conditions of plotting which must be observed

if the variation of an additive property with composition is to be expressed by a straight line were briefly summarised.

*"A Method of Rock-Analysis Diagrams Based on Statistics."* By W. A. Richardson.

Oxide variation diagrams, similar to those employed by Dr. Harker, can be used for expressing the chemical relations of rock groups and individuals. The diagrams obtained from plotting Iddings' selected analyses gave the maximum variation for all rocks.

*"Identity of Trechmann's 'β-tin' with Stannous Sulphide."* By L. J. Spencer.

A re-examination of the original material described by C. O. Trechmann in 1879 as an orthorhombic modification of tin proved that he made his crystallographic determinations on crystals of one kind (viz., stannous sulphide), whilst the chemical analysis was made on crystals of another kind (viz., metallic tin). Tin is therefore dimorphous and not trimorphous, "white tin" being tetragonal, and "grey tin" cubic. Orthorhombic crystals of stannous sulphide (SnS) and tetragonal crystals of iron stannide ($FeSn_3$) from tin furnaces, and rhombohedral crystals of tin arsenide ($Sn_3As_2$) isolated from a tin-arsenic alloy were described.

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## THE SOCIETY OF GLASS TECHNOLOGY.

*Wednesday, January 19, 1921.*

Dr. M. W. Travers, F.R.S., in the Chair.

The Fortieth Meeting of the Society of Glass Technology was held in the Mappin Hall, Applied Science Department, The University, Sheffield.

The first paper presented was entitled :—

*"The Rate of Change of Glass Composition in a Tank Furnace following a Change in the Batch Composition."* By John Currie, M.A.

In this paper, which was given by Prof. W. E. S. Turner, the author stated that the tank furnace in question had a dead-weight capacity of 106 tons. During six working days in the week, filling on took place every two hours, the quantity added being made up of 30cwt. of batch and 4cwt. of cullet, derived directly from the working end. Originally, the metal in this tank was used for bottles made on Forster machines. In place of these there were installed semi-automatic O'Neill machines, with Hartford-Fairmont feeder. It was thus necessary to produce a glass of lower melting point and slower rate of setting. The batch was altered accordingly, so as to reduce the percentage of lime, at the same time increasing the percentage of alkali in the glass. At various dates after the new batch was put into use, a sample bottle was taken for analysis, and the density of the glass was also determined.

The main fact established in the paper was that a period of nearly three months was required to effect a radical change in the composition of the tank. After that period, the composition of the glass was nearly identical with that calculated from the new batch, the percentage of lime being 7·42 as compared with 6·78 in the theoretical composition.

The discussion that folowed this paper was exceptionally interesting, those taking part being the Chairman, Messrs. R. L. Frink, W. J. Rees, G. Simpson, J. H. Davidson, A. E. Hill, J. Connolly, and Th. Teisen. In the absence of the author, Prof. Turner replied.

Two other papers were presented, namely :—

(a) *"Problems arising in Tank Furnace Practice through Shortage of Saltcake."* By Prof. W. E. S. Turner.

(b) *"The Relative Advantages and Disadvantages of Limestone, Burnt Lime, and Slaked Lime as Batch Materials."* By F. W. Hodkin, B.Sc., and Prof. W. E. S. Turner.

These two papers were taken together, and presented by Prof. Turner. The relative advantages of saltcake and soda ash were discussed. It was pointed out that soda ash was generally much purer than saltcake, that it gave glass a considerably greater proportion of its weight than did saltcake, and that soda ash batch would melt more rapidly and readily than a saltcake batch. It was also alleged that saltcake had a more corrosive action than soda ash on the refractory materials of the furnace. Further, soda ash was usually transported on the railways more carefully than saltcake. The price had also to be considered, and an answer given to the question as to what happened when saltcake could not be got. Various substitutes had been tried with success. In some cases one-half or two-thirds of the saltcake had been replaced by a corresponding amount of soda ash. Attention was directed to an observation made by Mr. Golstharp, chemist to the Pittsburgh Plate Glass Co., U.S.A., to the effect that a good clear glass, having more than a certain lime content, could not be made with a wholly soda ash batch.

A number of lantern slides were presented showing the results of experiments made with small melts in which there were tried soda ash and saltcake batches, and also a mixture of these. In these experiments, they had tried in turn as the source of the alkali in the glass (1) limestone, (2) burnt lime, and (3) slaked lime. What resulted depended in a considerable degree upon the nature or form in which the lime was placed in the batch. In addition, there were other factors. Burnt lime may be expensive, but the burning of lime did not get rid of organic matter which had a reducing action in the tank, and therefore tended to make the colour poor. On the other hand, there were difficulties in handling burnt lime, while it also readily absorbed moisture and carbon dioxide. Limestone tended to make a batch more expensive, but when melted it gave off a considerable quantity of gas, which helped mechanically to stir up the glass, thereby giving greater homogeneity.

A discussion followed, in which there took part the Chairman, Messrs. W. J. Rees, R. L. Frink, G. Simpson, and J. Connolly. Mr. Hodkin and Prof. Turner replied.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. clxxi., No. 23, December 6, 1920.

Spectrum Analysis. Table of the most persistent lines of the elements, which should help in analysis.—M. A. de Grammont.—This work is the outcome of work carried out by the author during the last few years for many industries and Government Departments. The *raies ultimes* are designated by the symbols $_{u1}$, $_{u2}$, $_{u3}$, showing their order of persistence, $_{u1}$ being the last to disappear. The dominant lines are printed in heavy type, and those which are next in order are printed in ordinary type. The wave-lengths in the table are expressed in international Angström units. A certain number of the visible lines, principally those lower than 4800, have been placed in the column *crown uviol glav spectrograph* because they have been determined with this apparatus.

*Chemical Notices from Foreign Sources.*—The Dominant Lines in the Spectrums of the Elements.

| | | | By Photography. | |
|---|---|---|---|---|
| | | *Visible Portion.* | *"Uviol Crown" Glav Spectrograph.* | *Quartz Spectrograph* |
| Aluminium ... | | 6245·1 ; 6233·8 ... ... ... | **3961·5**$_{u1}$; **3944·0**$_{u}$ ... ... ... | 3092·7 , 3082·2 |
| Antimony ... | | | 3267·5 ; 3232·5 ... ... ... | **2598·1**$_{u}$ , **2528·5**$_{u}$ , 2311·5 |
| Argon ... ... | (1) | | | |
| Arsenic ... | | | | 2860·5 , **2780·2**$_{u}$ ; 2745·0 ; **2349·8**$_{u}$ , 2288·1 |
| Barium ... | | 5535·5 ... ... ... ... ... | **4934·1**$_{u2}$ ; **4554·0**$_{u1}$ ; 3891·8 ... | 2335·3 |
| Bismuth ... | | 4722·5 ... ... ... ... ... | | **3067·7**$_{u1}$ ; 2989·0 ; 2938·3 ; **2898·0**$_{u2}$ , 2780·5 |
| Boron... ... | | | 3451·4 ... ... ... ... ... | **2497·7**$_{u}$ ; **2496·8**$_{u}$ |
| Bromine ... | (2) | | | |
| Cadmium ... | | 6438·5 , 5085·8 , 4800·0... ... | 3610·5 ; 3261·1 ... ... ... | 2748·6 ; **2288·0**$_{u2}$ ; **2265·0**$_{u1}$ ; 2144·4 |
| Cæsium ... | | | **4593·2**$_{u}$ ; **4555·4**$_{u}$ ... ... ... | |
| Calcium ... | | | **4226·7**$_{u3}$ ; **3968·5**$_{u2}$ ; **3933·7**$_{u1}$ | |
| Carbon ... | | | 4266·9 ... ... ... ... ... | **2478·6**$_{u}$ ; 2296·9 |
| Cerium ... | (4) | | 4186·6 ; **4040·9**$_{u}$ ; **4012·6**$_{u}$ ... | |
| Chlorine ... | (2) | | | |
| Chromium ... | | 5208·4 , 5206·1 ; 5204·5... ... | 4289·7 , 4274·8 , **4254·3**$_{u}$ ; **3605·3**$_{u}$ ; **3593·5**$_{u}$ ; 3578·7 | |
| Cobalt... ... | | 5353·5 ; 5342·7 ... ... ... | **3453·5**$_{u}$ ; **3405·1**$_{u}$ ... ... ... | **2388·9**$_{u1}$ : **2378·6** , 2363·8 ; 2311·6 ; 2307·9 ; 2286·2 |
| Columbium | | | 4101·0 ; **4079·7**$_{u}$ ; **4059·0**$_{u}$ ; 3358·4 ... ... ... ... | |
| Copper ... | | 5218·2 . 5153·3 ; 5105·6... ... | **3274·0**$_{u2}$ ; **3247·5**$_{u1}$ ... ... ... | |
| Dysprosium | (1) | | | |
| Erbium ... | (4) | | 3906·3 ; 3692·7 ; 3499·1... ... | |
| Europium ... | | | 4205·1 ; **4129·8** ... ... ... | |
| Fluorine ... | (2) | | | |
| Gadolinium | (1) | | | |
| Gallium ... | | | **4172·1**$_{u1}$ , 4033·0 ... ... ... | |
| Germanium | | | **3269·5**$_{u2}$ ... ... ... ... ... | **3039·1**$_{u1}$ , 2651·4 |
| Glucinum ... | | | 3321·4 ; 3321·1 ... ... ... | **3131·1**$_{u1}$ , **3130·4**$_{u}$ |
| Gold ... ... | | 6278·2 : 5837·4 ; 4792·6... ... | | 2802·2 , **2676·0**$_{u1}$ ; **2428·0**$_{u}$ |
| Helium ... | (1) | | | |
| Holmium ... | (1) | | | |
| Hydrogen ... | | **6562·8**$_{u}$ ... ... ... ... ... | | |
| Indium .. | | | **4511·4**$_{u1}$ ; **4101·8**$_{u2}$ ... ... ... | |
| Iodine ... ... | (2) | | | |
| Iridium ... | (4) | | **3513·7**$_{u}$ ; 3437·1 , **3220·8**$_{u}$ ... | |
| Iron ... ... | | 4404·3 . 4383·6 ... ... ... | 4045·8 ; 3820·4 ; 3737·1 , 3734·9 , 3570·2 ; 3565·4 | **2755·7**$_{u}$ , **2749·3**$_{u}$ , **2739·6**$_{u}$ **2395·6**$_{u2}$ ; **2382·0**$_{u1}$ |
| Krypton ... | (1) | | | |
| Lanthanum | (4) | | 4333·8 , 4086·7 , 3995·8 ; 3988·5 ; **3949·1**$_{u}$ ... ... | |
| Lead... ... | | 5608·9 ; 5005·5 ... ... ... | **4057·8**$_{u1}$ ; **3683·5**$_{u2}$ ; 3639·6 ... | 2614·2 ; 2203·6 , 2175·8 |
| Lithium ... | | **6707·9**$_{u}$ ... ... ... ... ... | **4602·2**$_{u}$ ... ... ... ... ... | |
| Lutecium ... | (1) | | | |
| Magnesium... | | 5183·6 ; 5172·7 ; 5167·3... ... | 3838·3 ; 3832·3 ... ... ... | **2852·1**$_{u1}$ (1) ; **2802·7**$_{u2}$ ; **2795·5**$_{u3}$ |
| Manganese... | | 4283·6 ; 4783·5 ; 4754·1... ... | 4034·5 ; 4033·1 ; **4030·9**$_{u2}$ ... | 2605·7 ; **2593·7**$_{u}$ ; **2576·2**$_{u1}$ |
| Mercury ... | | 5460·7 ; 4358·3 ... ... ... | | **2536·5**$_{u}$ |
| Molybdenum | | 5570·5 ; 5533·2 ; 5506·5... ... | **3903·0**$_{u}$ (3) : **3864·1**$_{u}$ ; **3798·3**$_{u}$ (3) ; 3635·2... ... | |
| Neodymium | (3) | | 4303·6 ; 4177·3 ; 3951·2... ... | |
| Neon ... ... | (1) | | | |

| | | Visible Portion. | By Photography. "Uviol Crown" Glav Spectrograph. | By Photography. Quartz Spectrograph. |
|---|---|---|---|---|
| Nickel ... ... | | 5476·9, 5081·1, 4714·4... ... | 3619·4; 3524·5, 3515·1; 3414·8$_{u}$, 3380·6 ... ... | 2437·8; 2416·2$_{u1}$; 2316·1$_{u}$; 2303·0$_{u}$ |
| Nitrogen ... | (2) | | | |
| Osmium ... | (1) | | | |
| Oxygen ... | (2) | | | |
| Palladium ... | (4) | | 3634·7$_{u}$; 3609·6$_{u}$; 3421·2; 3404·6$_{u}$ ... ... ... ... | |
| Phosphorus | | | | 2555·0; 2553·3$_{u}$; 2535·6$_{u}$; 2534·0 |
| Platinum ... | (3) | 5475·8; 5390·8; 5301·6; 5227·6 | 3966·4$_{u}$; 3923·0; 3268·4 ... | 3064·7; 2929·8; 2734·0: 2659·4 |
| Potassium ... | | 5832·0; 5801·8; 5782·4... ... | 4047·2$_{u1}$; 4044·2$_{u}$; 3447·4; 3446·4 ... ... ... ... | |
| Præsodymium | (1) | | | |
| Radium .. | (1) | | (4285·9; 4682·2; 3814·5) (2)... | |
| Rhodium ... | (4) | | 3799·3, 3692·4; 3658·0; 3434·9$_{u}$ ... ... ... ... | |
| Rubidium ... | | | 4215·6$_{u2}$; 4201·8$_{u1}$ ... ... ... | |
| Ruthenium... | (4) | | 3499·0$_{u}$; 3436·7 ... ... ... | |
| Samarium ... | (1) | | | |
| Scandium ... | (4) | | 4246·9; 3651·9; 3613·8$_{u1}$; 3630 8$_{u}$ ... ... ... ... | |
| Selenium ... | (2) | | | |
| Silicon... ... | | 6370·9; 6346·8; 5057 0; 5042·3 | | 2881·6$_{u}$; 2528·5; 2516·1$_{u}$; 2506·9 |
| Silver ... ... | | 5465·5; 5209·1 ... ... ... | 3383·0$_{u2}$; 3280·7$_{u1}$ ... ... ... | 2437·7 |
| Sodium ... | | 5895·9$_{u1}$; 5890·0$_{u1}$ ... ... ... | 3303·0$_{u2}$, 3302·4$_{u2}$ ... ... ... | |
| Strontium ... | | | 4607·3$_{u}$; 4305 5; 4215·5$_{u2}$, 4077 8$_{u1}$ ... ... ... ... | |
| Sulphur ... | (2) | | | |
| Tantalum ... | (3) | 6045·5, 5997·4 ... ... ... | 3631·9; 3406·9; 3318·8; 3311 2$_{u}$ ... ... ... | 2963·4 |
| Tellurium ... | | | | 2769·8; 2530·8, 2385·8$_{u1}$; 2383 3$_{u2}$ |
| Terbium ... | (1) | | | |
| Thallium ... | | 5350·5$_{u1}$ ... ... ... ... ... ... | 3575·7$_{u2}$; 3519·2; 3229·8 ... | 2767·9 |
| Thorium ... | (4) | | 4019·1; 3601·1, 3539·6... ... | |
| Thulium ... | (1) | | | |
| Titanium ... | | green group (5014.3 to 4981.8) | 3372·8$_{u}$: 3361·2$_{u}$; 3349·4$_{u1}$... | |
| Tin ... ... | | 524·7... ... ... ... ... ... ... | 3801·0; 3330·6; 3262·3$_{u}$ ... | 2863·3$_{u}$; 2840·0; 2706·5 |
| Tungsten ... | (3) | | 4302 4$_{u1}$; 4294·7; 4008·8$_{u}$; 3613·8; 3215·6$_{u}$ ... ... | 2397·1 |
| Uranium ... | (2) | | | |
| Vanadium ... | (3) | | 4408·5; 4379 2; 3185·4, 3184·0; 3183·4 ... ... | 3110·7; 3102·3, 3093·1 |
| Xenon ... ... | (1) | | | |
| Neoytterbium | (4) | | 3988·0$_{u2}$; 3694·2$_{u1}$; 3289·4 ... | |
| Yttrium ... | (4) | | 3774·3$_{u2}$; 3710·3$_{u1}$; 3633·1; 3600·7$_{u3}$; 3242·3 ... ... | |
| Zinc ... ... | | 6362·3 ... ... ... ... ... | 4810·5$_{u3}$; 4722·2$_{u2}$; 4680·2; 3345·0$_{u1}$ ... ... ... ... | 2138·5 |
| Zirconium ... | | blue group (4815·5 to 4687·8) | 3496·2$_{u}$; 3438·2; 3392·0$_{u1}$ ... | |

(1) Not studied by the Author.
(2) Does not give either the "raies ultimes" or the dominant lines.
(3) In course of study; provisional results.
(4) Studied only in the crown uviol; provisional results.
(1) Masked by Sodium 2852·8.
(2) Runge and Precht.
(3) Masked by the Iron lines.

## MEETINGS FOR THE WEEK.

*Monday, February* 7, 1921.

Royal Institution, 5. (General Meeting).
Society of Chemical Industry, 8.

*Tuesday, February* 8.

Royal Institution, 3. "The British Soldier since the Restoration—In War," by Hon. J. W. Fortescue.
Institution of Electrical Engineers, 7. (At Leeds).
Institute of Metals, 8. (At Glasgow).
Royal Society of Arts, 8. "The Problem of Unemployment," by E. C. de Segunds.

*Wednesday, February* 9.

Conjoint Board, 3.
Royal Society of Arts, 4.30.

*Thursday, February* 10.

Royal Institution, 3. "Oceanography—Problems of the Plankton," by Prof. W. A. Herdman.
Society of Chemical Industry. (At Birmingham).
Institute of Chemistry. (At Liverpool).
Optical Society, 7.30.

*Friday, February* 11.

Royal Institution, 9. "Isotopes and Atomic Weights," by Dr. F. W. Aston.
Physical Society, 5. (Annual Meeting).
Faraday Society and Manchester Literary and Philosophical Society, 6 30. (At Manchester).

*Saturday, February* 12.

Royal Institution, 3. "Spectroscopy—Experimental Spectroscopy," by A. Fowler.

# THE CHEMICAL NEWS.

VOL. CXXII., No. 3174.

## EDITORIAL.

WE have recently drawn attention to the importance of glassware in the chemical industry, and to the efforts that are being made by British glass manufacturers to render the country independent of foreign supplies.

The Association of British Chemical Manufacturers have recently issued a statement pointing out the gravity of the situation as regards the production of fine chemicals which we are glad to publish, as these matters are of supreme national importance if we are to hold our own in the near future. Recent developments in Germany, both in home politics and in trade propaganda enhance the importance of increasing vigilance at the present moment

### A KEY INDUSTRY.

Are Britain's Laboratories in peril? The Association of British Chemical Manufacturers draws attention to the present position of the Fine Chemical Industry.

The next month or so will decide whether, in the years to come, Great Britain is to make fine chemicals for all the world, or whether we and the other nations are once more to turn to Germany for our laboratory and photographic chemicals, for essential drugs like antipyrin, phenacetin, cocaine, salicylates, aspirin, salversan, and others.

The case against buying these fine chemicals from the Germans is not founded on any foolish post-war prejudice against trading with a former enemy. It is a matter of international principle only less grave than the surrender of the High Seas Fleet and the reduction of the German Army. To-day it should not be necessary to remind any British citizen that it was Germany's phalanx of expert chemists with their experienced workmen who gave her so tremendous an advantage in the early days of the struggle. That military asset was, of course, the direct consequence of the fact that Germany had been chemical maker to the world; nor for several reasons was it possible in those days to compete with the laboratories which in a night were to become munition factories. For one thing, Germany had built up what was practically a monopoly in the fine chemical industry because the raw materials for that industry are largely the bye-products of the dye-stuffs industry —by that time, of course, almost a German monopoly.

*Mobilising the Chemists.*—The war found her supreme, both in the necessary plant and in the knowledge, not readily acquired, of the most economical mode of production. But it did not leave her supreme; and it will be strange if we have since forgotten what we then learnt, namely, the unwisdom of leaving in the hands of any one nation the supply of drugs essential to our health, especially when that surrender places ready to her hand the plant needed for the manufacture of explosives and the chemists and the workmen skilled in its use.

The position amongst us to-day may be simply stated. During the war we assembled from our polytechnics, colleges, and universities, men who, after much striving and many failures, did arduously acquire not only a knowledge of the explosives which destroy life, but of certain drugs, such as phenacetin, salicylates, and salversan that save it. But the plant which was then rigged up was emergency plant; the methods were emergency methods—in the circumstances, naturally expensive. Are we for these reasons to permit our little army of chemist experts to be scattered? Are we to hand back to Germany an industry so lucrative in time of peace and potentially so formidable for war?

*The Making of Medicines.*—Or should we give ourselves a chance? It must not be imagined that our men have failed to make good. They have made good; or rather they are just on the point of doing so. The manufacture of research chemicals, of photographic chemicals, of synthetic perfumes and essences is each on the verge of commercial success. The manufacture of drugs has made immense strides; many; begun some time ago, have been brought to perfection; others had been added or were being added when the decision of Mr. Justice Sankey was dropped like a bomb into the thick of these experimentings. British manufacturers had proved that they could make fine chemicals as good as the fine chemicals of Germany, and they were slowly but quite surely bringing down the cost of making them, when suddenly the Order in Council prohibiting the importation of drugs was swept aside.

What has been the effect? Germany, it must be remembered, had long ago arrived at the point to which this new industry of ours was gradually struggling. She not only had her troops of industrial chemists; her plant was established and still intact; she had already made all the short cuts to cheap production. And in addition to these circumstances, the fact that the mark is now worth a penny instead of a shilling permits her to sell profitably on the British market at a price below our cost of actual manufacture.

*Wanted: A Breathing Space.*—Inevitably that means an end to the fine chemical industry amongst us; unless British firms be given a breathing space to prepare for competition on fair terms. Many such firms are at this moment clinging to the hope that the Key Industries Bill which has been promised as the first Government measure of the next session will even yet permit our country to become eventually the source of the world's fine chemical supply. Just as the making of fine chemicals is the complement to the making of dyestuffs, so is this Bill a pendant of the Dyestuffs Act, already approved by an overwhelming majority in the House of Commons.

There does not appear to be any weighty reason why we should send to other countries our coal tar, and other bye-products from the manufacture of dyes, to be made into chemicals by foreign labour in foreign plant erected by foreign capital. The only class amongst us who would benefit would be the handful of brokers who would get their commission out of selling over again such of the bye-products as came back to us in their manufactured state.

*The Gain to the Nation.*—On the other hand, the national advantages of a flourishing industry such as this will be apparent. Clearly, of course, it would reduce unemployment, add to the taxable income of the country and the rateable value of many cities. Nor need one labour the truism that every fine chemical works may at once in time of war, if unhappily that should ever come, be turned into a munitions factory with skilled chemists and workers complete. They are as necessary to the production of explosives as are steel workers to the production of battleships, and, while both groups of workers may happily never again in our time need to step forward in a national emergency, it is surely essential that they should be there at call, peacefully engaged meanwhile in endeavouring to pay off the National Debt. Indeed, excluding coal mining, the fine chemical industry yields the highest net value of output per head, and it employs the greatest proportion of salaried workers. It offers almost unrivalled scope to those upon whose education nowadays we spend so much. It rounds off that education without any subsidy, training, without cost, research chemists who in turn must add to the national wealth as they open up new paths of enterprise. In short, one may no more set a limit to the future of this industry than to its effect upon sister industries. It it be properly encouraged it will sow prosperity in the most unexpected corners of our whole field of commerce. The chemist is now a mighty ruler and discoverer, and the laboratory harnesses the energies of the earth either to save or to destroy, as the mind of men shall determine.

## CHLOROFORM SOLUTIONS OF HYDROGEN CHLORIDE.

By E. J. WILLIAMS.

IN an attempt to prepare a standard solution of hydrogen chloride in chloroform it was found that, on titration with standard alkali, concordant results could not be obtained for successive titrations even when the solutions obtained were largely diluted by the further addition of chloroform.

The solutions were prepared by passing dry hydrogen chloride through dry chloroform purified from methylated chloroform. The minimum concentration of hydrogen chloride present was obtained by running a measured portion of the solution from a burette into excess of standard sodium hydroxide contained in a glass-stoppered bottle, shaking thoroughly, and then running in standard hydrochloric acid to determine the excess of alkali The chloroform solution could not be measured by a pipette, since the pressure of the hydrogen chloride caused the solution to drip out of the pipette.

The treatment accorded to the solutions and the results obtained are indicated in the subjoined table. All solutions were at laboratory temperature (10° C.).

| Method of preparation. | Grams Hydrogen chloride per litre found. |
|---|---|
| (1) Original chloroform (a) .. .. ... . | 0·00 |
| (2) Dry hydrogen chloride passed through (1) for half-an-hour (b) . ... | 9·50 |
| (3) Solution (2) shaken very slightly and again titrated ... ... . . ... ... .. | 7·30 |
| (4) Dry air slowly aspirated through solution (2) for two hours (a) ... . ... | 0·00 |
| (5) 25 cc. of solution (2) diluted to 50 cc. with chloroform (c) .. .. . .. | 0·68 |
| (6) Solution (5) refluxed for three hours on water-bath (a) .. ... ... ... ... | 0·00 |
| (7) Dry air slowly aspirated through solution (5) for two hours (a) ... ... . . | 0·00 |
| (8) Dry hydrogen chloride passed through (1) for two hours (d) ... ... ... .. | 9·80 |
| (9) 50 cc. of solution (8) diluted to 250 cc. with chloroform (e) . . ... ... .. | 1·60 |
| (10) Solution (8) kept in desiccator over solid caustic soda for 24 hours (a) .. | 0·00 |

(a) Gave no turbidity with silver nitrate.
(b) Liquid fumed strongly in air.
(c) Solution still fumed in air.
(d) Solution fumed strongly in air and repeatedly blew stopper out of bottle while standing.
(e) Fumed strongly.

*Summary.*

1. Hydrogen chloride can be absorbed by chloroform up to a concentration of about 10 grms. per litre.

2. Equilibrium between solvent and solute is unstable, and unless the solution is kept in a closed vessel the gas passes completely out of solution.

Royal Grammar School Newcastle-on-Tyne.

## THE RELATIVE VOLUMES OF THE CHEMICAL ELEMENTS.

By HAWKSWORTH COLLINS.

SINCE it has been proved that it is impossible to compare the relative volumes of substances at their boiling points, but that it is possible to do so at some fixed temperature, 15° C. has been selected in this investigation, because the great majority of specific gravities of substances have been found experimentally at about this temperature.

Whenever the experimental specific gravities of substances have not been given at this temperature, their values have been reduced in a uniform manner in accordance with the experimental data, with regard to similar substances.

Since experimentalists very seldom agree to more than three figures in their determination of the specific gravity of a substance, and since it will be seen that the theoretical results nearly always agree with the experimental to three figures, it is evident that the theory is as exact as possible.

The importance of the matter consists in the fact that it throws an entirely new and strong light of mathematical exactitude upon every substance in existence, and ultimately leads to the

demonstration of numerous discoveries concerning Optical Refractivity, Magnetic Rotation, Heat of Combustion, Heat of Formation, &c.

It is necessary to draw special attention to the following statement, which has sometimes been ignored by scientists.—*There is no assumption of any kind whatever in any portion of the following theory.*

The atomic weights of Cl, Br, I, N, H, C, O, S, are taken as 35·5, 79, 127, 14, 1, 12, 16, and 32 respectively.

When it has been definitely proved experimentally that the atomic weights of Cl are 35 and 36, and of Br 79 and 81, the relative volumes of these two elements will have to be recalculated from new experimental data. Meanwhile it is evident that the two volumes of Cl must be very nearly equal, otherwise it would have been impossible to obtain the following results. Similar remarks apply to Br.

When the molecular weight of a substance is divided by the specific gravity, the result is its molecular volume.

The deductions are frequently given before the facts which lead up to them, for the sake of convenience.

First deduction.—*The relative volume of methylene* ($CH_2$) *at* 15° *C. is* 16·42. The truth of this is apparent by comparing any two of the following compounds which differ by $CH_2$, or a multiple of $CH_2$.

Second deduction.—The experimental facts concerning the following 149 molecules demonstrate that the relative volumes at 15° C. of the following atoms or groups are:—

| | | | |
|---|---|---|---|
| Cl | 23·01 | $CO_2CH_3$ | 49·71 |
| Br | 27 | $CO_2C_2H_5$ | 66·13 |
| I | 32·75 | $CO_2C_3H_7$ | 82·55 |
| $NH_2$ | 16·42 | $CO_2C_4H_9$ | 98·97 |
| CN | 23·96 | $CO_2C_5H_{11}$ | 115·39 |
| $N_3$ | 32·63 | $C_6H_5$ | 77·48 |
| $NO_2$ | 26·74 | $C_6H_5$ | 74·45 |
| $NO_3$ | 34·27 | OH | 13·29 |
| SH | 25·48 | OH | 16·21 |
| $C_2H_3$ | 41·87 | $CCl_3$ | 69·74 |
| $C_2H_2$ | 28·89 | CO.OH | 23·8 |
| $C_2H$ | 31·25 | | |

The relative volumes obtained for the groups $C_2H$, $C_2H_2$ and $CH_2$ may appear to be absurd, but proofs will be given later that they are correct.

There are two values obtained for each of the groups $C_6H_5$ and OH It would have been much easier to have ignored the two values and to have taken the mean value in each case, but, since we wish to obtain the exact truth and not merely the approximate truth, these apparently contradictory values are purposely introduced at the commencement of the theory.

| | Name and Chem. Formula. | Vols of Parts. | Theor. S.G. | Observed S.G. |
|---|---|---|---|---|
| | Methylene chloride Cl—$CH_2$—Cl | 23·01 — (16·42) — 23·01 | 1·361 | 1·378 0° T. ∴ 1·361 15° |
| | Ethylene Cl Cl—$(CH_2)_2$—Cl | 23·01 — $(16·42)_2$— 23·01 | 1·255 | 1·252 20° B. 1·256 12° Re |
| | Trimethylene Cl Cl—$(CH_2)_3$—Cl | 23·01 — $(16·42)_3$— 23·01 | 1·186 | 1·189 18° Fr. |
| | Hexylene Cl Cl—$(CH_2)_6$—Cl | 23·01 — $(16·42)_6$— 23·01 | 1·072 | 1·087 20° C. 1·053 11° H. |
| 5 | Methylene bromide Br—$CH_2$—Br | 27·00 — (16·42) — 27·00 | 2·442 | 2·084 11° St. 2·5 15° P. |
| | Ethylene Br Br—$(CH_2)_2$—Br | 27·00 — $(16·42)_2$— 27·00 | 2·142 | 2·128 13° D. 2·164 21 Re. |
| | Trimethylene Br Br—$(CH_2)_3$—Br | 27·00 — $(16·42)_3$— 27·00 | 1·937 | 1·923 Fr. 1.982 15° P. |
| | Hexylene Br Br—$(CH_2)_6$—Br | 27·00 — $(16·42)_6$— 27·00 | 1·587 | 1°581 19° He. 1·6 13° Be. |
| | Heptylene Br Br—$(CH_2)_7$—Br | 27·00 — $(16·42)_7$— 27·00 | 1·515 | 1·515 18° T. |
| 10 | Ethylene chlorobromide Cl—$(CH_2)_2$—Br | 23·01 — $(16·42)_2$— 27·00 | 1·720 | 1·705 11° Mo. 1·7 18° H. |
| | Methylene iodide I—$(CH_2)$—I | 32·75 — (16·42) — 32·75 | 3·271 | 3 285 15° P. 3·23 16° B. |
| | Trimethylene iodide I—$(CH_2)_3$—I | 32·75 — $(16·42)_3$— 32·75 | 2·579 | 2·576 15° P. |
| | Chloriodomethane Cl—$(CH_2)$—I | 23·01 — (16·42) — 32·75 | 2·445 | 2·444 14° Sk. |
| | Ethylene chloriodide Cl—$(CH_2)_2$—I | 23·01 — $(16·42)_2$— 32·75 | 2·15 | 2·151 0° Si. |

ABBREVIATIONS.—A, Anschutz; B, Bruhl; Ba, Bauer; Be, Beresty; Bo, Boughton: Br, Brauns; Bt, Berthelot; By, Bruylants; C, Cahours, Ca, Cannizzaro; Car, Carrara; Cl, Clermont; C.K., Chemiker Kalendar; Co, Conrad; Ch, Chavanne; Cr Carlet; D, D'Arcet; De, Delffs, Dh, De Heen; Dv, Deville, E, Engler, Er, Erlenmeyer; Ei, Eisenloh, F, Fittig; Fa, Fahlberg; Fd, Friedel; Fh, Fruhling, Fo, Forster; Fr, Freund; G Gladstone; Ga, Gartenmeister; Ge, Gehring; G.T., Garzarolli-Thurnlackh; Gu, Gustavson; H, Henry; Hg, Hodgkins; He, Hecht; Hl, Hell; Ho, Hofmann; I, International Constants; Is, Istrati, K, Kahlbaum; Ke, Kekule; Ko, Kopp; Kr, Krafft; L, Linnemann; Le, Lescher; La, Laurent; Lb, Lieben; Li, Limpricht; M, Mendelejeff; Mo, Montgolfier; J, Jungfleisch; Ma, Malaguti; Mr, Markownikoff; P, Perkin, Pa, Pariselle; Pi, Pickard; Pl, Plimpton; Pt, Paterno; R, Romburgh; Ra, Radziszewski; Rb, Reboul; Re, Regnault; Ru, Rugheimer, S, Schroder; Sa, Saytzeff, Sb Sabanejeff; Sc, Schorlemmer; Sch, Schall; Sh, Schiff; Si, Simpson, Sk, Sakurai, Sl, Silva; Sm, Stohmann; So, Sokoloff; Sr, Schreiner, St, Steiner; Sw, Schwers; T, Thorpe; Tr, Truchot; V, Vogt; Va, Van Nostrand; W, Wurtz; We, Werner, Wi, Wiens; Wg, Weger; Wr, Wroblevsky; Z, Zander.

| | Name and Chem. Formula. | Vols of Parts. | Theor. S.G. | Observed S.G. |
|---|---|---|---|---|
| 15 | Ethylene bromiodide $Br-(CH_2)_2-I$ ... ... | 27·00 — $(16·42)_2$ — 32·75 | 2·527 | 2·514 30°Fd. 2·7 1° Rb. |
| | Pentamethylene diamine $NH_2-(CH_2)_5-NH_2$ | 16·42 — $(16·42)_5$ — 16·42 | 0·887 | 0·885 15°/4 Va. |
| | Chloracetonitril $Cl-CH_2-CN$ ... ... | 23·01 — (16·42) — 23·96 | 1·191 | 1·193 20° E. |
| | β-Triazoethylamine $N_3-(CH_2)_2-NH_2$ ... | 32·63 — $(16·42)_2$ — 16·42 | 1·050 | 1·049 16°Fo. ∴1·050 15° |
| | γ-Triazopropylamine $N_3-(CH_2)_3-NH_2$ ... | 32·63 — $(16·42)_3$ — 16·42 | 1·017 | 1·004 25°/4 I. ∴ 1·014 15° |
| 20 | Ethylene chloronitrin $Cl-(CH_2)_2-NO_3$ ... | 23·01 — $(16·42)_2$ — 34·27 | 1·393 | 1·378 21° H. ∴ 1·385 15° |
| | Ethylene dinitrate $NO_3-(CH_2)_2-NO_3$ | 23·01 — $(16·42)_2$ — 34·27 | 1·500 | 1·51 4° Va. ∴ 1·50 15° |
| | Ethylene mecaptan $SH-(CH_2)_2-SH$ .. | 25·48 — $(16·42)_2$ — 25·48 | 1·122 | 1·123 23° We. |
| | Diallyl $C_2H_3-(CH_2)_2-C_2H_3$ | 41·87 — $(16·42)_2$ — 41·87 | 0·703 | 0·707 0° Z. 0·698 12° Sh. |

In the following, M stands for methylene ($CH_2$) both in the formula and in the relative volumes Its volume is always 16·42.

| | Name and Chem. Formula. | Vols of Parts. | Theor. S.G. | Observed S.G. |
|---|---|---|---|---|
| | Allyl chloride $C_2H_3-M-Cl$ ... ... ... | 41·87 — M — 23·01 | 0·941 | 0·938 20° B. 0·944 15° P. |
| 25 | Chloramylene $C_2H_3-M_3-Cl$ ... ... ... | 41·87 — $M_3$ — 23·01 | 0·916 | 0·999 0° Ba. 0·872 5° By. |
| | Chlorhexylene $C_2H_3-M_4-Cl$ ... ... ... | 41·87 — $M_4$ — 23·01 | 0·907 | 0·904 11° H. |
| | Allyl bromide $C_2H_3-M-Br$ ... ... .. | 41·87 — M — 27·00 | 1·407 | 1·421 15° P. 1·398 20° B |
| | Bromhexylene $C_2H_3-M_4-Br$ ... ... ... | 41·87 — $M_4$ — 27·00 | 1·204 | 1·203 15° He |
| | Allyl iodide $C_2H_3-M-I$ ... ... ... | 41·87 — M — 32·75 | 1·845 | 1·846 15° R. 1·848 12° L. |
| 30 | Diallyl hydriodate $C_2H_3-M_4-I$ ... ... ... | 41·87 — $M_4$ — 32·75 | 1·497 | 1·497 0° W. |
| | Allylamine $C_2H_3-M-NH_2$ ... ... | 41·87 — M — 16·42 | 0·763 | 0·769 17°·5 G. |
| | Dibenzyl $C_6H_5-M_2-C_6H_5$ .. . | 74·45 — $M_2$ — 74·45 | 1·001 | 1·002 14° Li. ∴ 1·001 15° |
| | Diphenyl methane $C_6H_5-M-C_6H_5$ ... .. | (77·48 / 74·45) — M — 74·45 | 1·007 | 1·006 25°/25 K. |
| | Diphenyl propane $C_6H_5-M_3-C_6H_5$ ... .. | (77·48 / 74·45) — $M_3$ — 74·45 | 0·982 | 0·996 0° Sl. ∴ 0·983 15° |
| 35 | Benzyl chloride $C_6H_5-M-Cl$ ... .. ... | 74·45 — M — 23·01 | 1·111 | 1·113 Ca. 1·103 18° I. |
| | Benzyl chloride $C_6H_5-M-Cl$ ... ... ... | (77·48 / 74·45) — M — 23·01 | 1·096 | 1·099 7° G. |
| | Chlorethylbenzene $C_6H_5-M_2-Cl$ ... ... ... | 77·48 — $M_2$ — 23·01 | 1·054 | 1·068 0° Is. ∴ 1·055 15° |
| | Benzyl bromide $C_6H_5-M-Br$ ... ... ... | 74·45 — M — 27·00 | 1·442 | 1·438 22° Ke. ∴ 1·445 15° |
| | Benzyl iodide $C_6H_5-M-I$ ... ... ... | (77·48 / 74·45) — M — 32·75 | 1·742 | 1·734 25° Lb. ∴ 1·745 15° |
| 40 | Benzylamine $C_6H_5-M-NH_2$ ... ... | 74·45 — M — 16·42 | 0·997 | 0·990 14° Li. |
| | Benzylamine $C_6H_5-M-NH_2$ ... ... | (77·48 / 74·45) — M — 16·42 | 0·984 | 0·986 15°/15 Va. |
| | β-Phenylethylamine $C_6H_5-M_2-NH_2$ ... ... | 77·48 — $M_2$ — 16·42 | 0·955 | 0·952 20°/4 I. ∴ 0·955 15° |
| | β-Phenylethylamine $C_6H_5-M_2-NH_2$ ... .. | (77·48 / 74·45) — $M_2$ — 16·42 | 0·966 | 0·959 25°/25 K. ∴ 0·965 15° |
| | β-Phenylethylamine $C_6H_5-M_2-NH_2$ ... ... | 74·45 — $M_2$ — 16·42 | 0·979 | 0·972 25° I. ∴ 0·979 15° |
| 45 | Benzyl cyanide $C_6H_5-M-CN$ ... ... | 74·45 — M — 23·96 | 1·018 | 1·015 18° Ho. ∴ 1·018 15° |
| | Phenylpropionitril $C_6H_5-M_2-CN$ ... ... | 74·45 — $M_2$ — 23·96 | 1·00 | 1·0014 18° Ho. |
| | Ethylene diacetate $CH_3CO_2-M_2-CO_2CH_3$ | 49·71 — $M_2$ — 49·71 | 1·104 | 1·109 14° Sw. |

| No. | Name and Chem. Formula. | Vols of Parts. | Theor. S.G. | Observed S G. |
|---|---|---|---|---|
| | Propylene diacetate<br>$CH_3CO_2$—$M_3$—$CO_2CH_3$ | 49·71 — $M_3$— 49·71 | 1·076 | 1070 19° Rb. ∴ 1·074 15° |
| | Methyl suberate<br>$CH_3CO_2$—$M_6$—$CO_2CH_3$ | 49·71 — $M_6$— 49·71 | 1·020 | 1·014 18° La. ∴ 1·017 15° |
| 50 | Methyl chloracetate<br>Cl—M— $CO_2CH_3$ ... ... | 23·01 — M — 49·71 | 1·22 | 1·22 15° H. |
| | Ethylene aceto-chloride<br>Cl—$M_2$—$CO_2CH_3$ ... ... | 23·01 — $M_2$— 49·71 | 1·161 | 1·178 0° Si. ∴ 1·163 15° |
| | Hexylene aceto-chloride<br>Cl—$M_6$—$CO_2CH_3$ ... ... | 23·01 — $M_6$— 49·71 | 1·042 | 1·04 6° H. |
| | Octylene aceto-chloride<br>Cl—$M_8$—$CO_2CH_3$ ... ... | 23·01 — $M_8$— 49·71 | 1·0118 | 1·011 18° Cl. |
| | Methyl brombutyrate<br>Br—$M_3$—$CO_2CH_3$ ... ... | 27·00 — $M_3$— 49·71 | 1·43 | 1·450 5° H. ∴ 1·438 15° |
| 55 | Acetoxyacetonitril<br>CN—M —$CO_2CH_3$ .. . . | 23·96 — M — 49·71 | 1·099 | 1 100 14° H. ∴ 1·099 15° |
| | Benzyl acetate<br>$C_6H_5$—M —$CO_2CH_3$ ... | 77·48 — M — 49·71 | 1·044 | 1·040 21° G. ∴ 1·045 15° |
| | Benzyl acetate<br>$C_6H_5$—M —$CO_2CH_3$ . | 74·45 — M — 49·71 | 1·067 | 1·062 15° Va. |
| | Allyl acetate<br>$C_2H_3$—M —$CO_2CH_3$ . . | 41·87 — M — 49·71 | 0·9259 | 0°9258 24°·5 G. |
| | Ethyl malonate<br>$C_2H_5CO_2$—M —$CO_2C_2H_5$ | 66·13 — M — 66·13 | 1°076 | 1·068 18° Co. ∴ 1 071 15° |
| 60 | Ethylene dipropionate<br>$C_2H_5CO_2$—$M_2$—$CO_2C_2H_5$ | 66·13 — $M_2$— 66·13 | 1·054 | 1·054 15° P. |
| | Ethyl succinate<br>$C_2H_5CO_2$—$M_2$—$CO_2C_2H_5$ | 66·13 — $M_2$— 66·13 | 1°054 | 1·072 0° Ko. 1·047 26° Ko. |
| | Ethyl suberate<br>$C_2H_5CO_2$—$M_6$—$CO_2C_2H_5$ | 66·13 — $M_6$— 66·13 | 0·997 | 0·991 15° Hl. 1·003 18° La. |
| | Ethyl sebate<br>$C_2H_5CO_2$—$M_8$—$CO_2C_2H_5$ | 66·13 — $M_8$— 66·13 | 0·979 | 0·968 15° P. 0·99 25° K. |
| | Ethyl chloracetate<br>Cl—M —$CO_2C_2H_5$ ... ... | 23·01 — M — 66·13 | 1·160 | 1·172 8° H. 1·158 20° B. |
| 65 | Et. β chlorpropionate<br>Cl—$M_2$—$CO_2C_2H_5$ .. . | 23·01 — $M_2$— 66·13 | 1·119 | 1 116 8° H. |
| | Et. chlorbutyrate<br>Cl—$M_3$—$CO_2C_2H_5$ . . ... | 23·01 — $M_3$— 66·13 | 1·087 | 1·052 20° B. 1·122 10° H. |
| | Et. bromacetate<br>Br—M —$CO_2C_2H_5$ ... ... | 27·00 — M — 66·13 | 1·515 | 1·525 18° G. 1·507 25° K |
| | Et. brombutyrate<br>Br—$M_3$—$CO_2C_2H_5$ .. . . | 27·00 — $M_3$— 66·13 | 1·362 | 1·363 5° H. |
| | Et. cyanacetate<br>CN—M —$CO_2C_2H_5$ . .. | 23·96 — M — 66·13 | 1·061 | 1·059 25° K. 1·067 13° H. |
| 70 | Et. allylacetate<br>$C_2H_3$—$M_2$—$CO_2C_2H_5$ ... | 41·87 — $M_2$— 66·13 | 0·91 | 0·922 0° W. ∴ 0·911 15° |
| | Et allyloctylate<br>$C_2H_3$—$M_8$—$CO_2C_2H_5$ .. | 41·87 — $M_8$— 66·13 | 0·886 | 0·883 15° P. |
| | Et oleate<br>$C_2H_3$—$M_{15}$—$CO_2C_2H_5$ ... | 41·87 — $M_{15}$— 66·13 | 0·875 | 0·875 15° P. |
| | Methyl ethyl succinate<br>$CH_3$—$CO_2$—$M_2$—$CO_2C_2H_5$ | 49·71 — $M_2$— 66·13 | 1·08 | 1·092 0° Wg. ∴ 1·08 15° |
| | Et. phenylacetate<br>$C_6H_5$—M —$CO_2C_2H_5$ ... | (77·48 / 74·45)— M — 66·13 | 1·035 | 1·029 25°/25 K. ∴ 1·035 15° |
| 75 | Benzyl propionate<br>$C_6H_5$—M —$CO_2C_2H_5$ . . | (77·48 / 74·45) — M — 66·13 | 1·035 | 1·036 16°·5 Co. |
| | Et hydrocinnamate<br>$C_6H_5$—$M_2$—$CO_2C_2H_5$ ... | (77·48 / 74·45)— $M_2$— 66·13 | 1·018 | 1·012 25°/25 K. ∴ 1·018 15° |
| | Et. phenpropionate<br>$C_6H_5$—$M_2$—$CO_2C_2H_5$ ... | (77·48 / 74·45)— $M_2$— 66·13 | 1·018 | 1·034 0° E. 1·015 20° B. |
| | Ethylene dibutyrate<br>$C_3H_7$—$CO_2$—$M_2$—$CO_2C_3H_7$ | 82·55 — $M_2$— 82·55 | 1·021 | 1·024 0° W. |
| | Ethylene butyro-chloride<br>Cl—$M_2$—$CO_2C_3H_7$ . . ... | 23·01 — $M_2$— 82·55 | 1·087 | 1·085 0° Si. |
| 80 | Pr. phenylacetate<br>$C_6H_5$—M —$CO_2C_3H_7$ ... | (77·48 / 74·45)— M — 82·55 | 1·017 | 1·014 18° Hd. ∴ 1·017 15° |
| | Benzyl butyrate<br>$C_6H_5$—M —$CO_2C_3H_7$ .. | (77·48 / 74·45) — M — 82·55 | 1·017 | 1·016 16° Co. ∴ 1·017 15° |

| | Name and Chem. Formula. | Vols of Parts. | Theor. S.G. | Observed S.G. |
|---|---|---|---|---|
| | Pr. phenpropionate $C_6H_5—M_2—CO_2C_3H_7$ ... | $\binom{77·48}{74·45}$ — $M_2$ — 82·55 | 1·003 | 1·015 0° Wg ∴ 1·002 15° |
| | Butyl chloracetate $Cl—M—CO_2C_4H_9$ ... ... | 23·01 — M — 98·97 | 1·087 | 1·081 15° Ge. |
| | Chlorethyl alcohol $Cl—M_2—OH$ ... . ... | 23·01 — $M_2$ — 10·21 | 1·219 | 1·201 19° Va. |
| 85 | Trimethylene chlorhydrin $Cl—M_3—OH$ ... ... ... | 23·01 — $M_3$ — 10·21 | 1·146 | 1·132 17° Tr. |
| | Octylene chlorhydrin $Cl—M_8—OH$ ... .. ... | 23·01 — $M_8$ — 10·21 | 0·999 | 0·987 31° Cl. ∴ 0·999 15° |
| | Ethylene cyanhydrin $CN—M_2—OH$ . .. .. | 23·96 — $M_2$ — 10·21 | 1·059 | 1·059 0° E. |
| | Butylene-1-ol-4 $C_2H_3—M_2—OH$ . . | 41·87 — $M_2$ — 10·21 | 0·848 | 0·848 17°/0 Pa. |
| | Benzyl alcohol $C_6H_5—M—OH$ . .. | $\binom{77·48}{74·45}$ — M — 10·21 | 1·053 | 1·051 15° Ko. 1·059 Ca. |
| 90 | Phenylethyl alcohol $C_6H_5—M_2—OH$ . . .. | 74·45 — $M_2$ — 10·21 | 1·038 | 1·034 21° C.K. ∴ 1·038 15° |
| | Benzyl carbinol $C_6H_5—M_2—OH$ ... ... | 74·45 — $M_2$ — 10·21 | 1·038 | 1·034 21° Ra. ∴ 1·038 15° |
| | Benzyl carbinol $C_6H_5—M_2—OH$ . .. | $\binom{77·48}{74·45}$ — M — 10·21 | 1·025 | 1·024 15° Va. |
| | Phenylpropyl alcohol $C_6H_5—M_3—OH$ ... . | 74·45 — M — 10·21 | 1·015 | 1·008 20° B. ∴ 1·013 15° |
| | Phenylbutanol $C_6H_5—M_4—OH$ ... ... | 77·48 — $M_4$ — 10·21 | 0·978 | 0·976 17°/4 I. ∴ 0·978 15° |
| 95 | Propyl glycollate $C_3H_7CO_2—M—OH$ ... | 82·55 — M — 10·21 | 1·081 | 1·084 Sr. |
| | Hexylene chlorhydrin $HO—M_6—Cl$ ... ... ... | 13·29 — $M_6$ — 23·01 | 1·012 | 1·018 11° H. ∴ 1·012 15° |
| | Trimethylene bromhydrin $HO—M_3—Br$ ... ... ... | 13·29 — $M_3$ — 27·00 | 1·541 | 1·537 20° Fh. 1·543 15° |
| | Hexylene bromhydrin $HO—M_6—Br$ ... ... ... | 13·29 — $M_6$ — 27·00 | 1·297 | 1·296 11° H. |
| | Ethylene monoacetate $HO—M_2—CO_2CH_3$ .. ... | 13·29 — $M_2$ — 49·71 | 1·085 | 1·0+ Va. |
| 100 | Et. glycollate $HO—M—CO_2C_2H_5$ ... | 13·29 — M — 66·13 | 1·085 | 1·083 23° Va. 1·107 Sr. |
| | Glycol $HO—M_2—OH$ ... ... ... | 13·29 — $M_2$ — 10·21 | 1·101 | 1·125 0° Va. ∴ 1·111 15° |
| | Trimethylene glycol $HO—M_3—OH$ ... ... ... | 13·29 — $M_3$ — 10·21 | 1·045 | 1·062 0° Z. ∴ 1·048 15° |
| | Dipropargyl $C_3H—M_2—C_3H$ ... ... | 31·25 — $M_2$ — 31·25 | 0·818 | 0·81 18° H. 0·82 Bt. |
| | Propargyl chloride $C_3H—M—Cl$ .. ... ... | 31·25 — M — 23·01 | 1·054 | 1·045 5° H. |
| 105 | Propargyl bromide $C_3H—M—Br$ ... ... ... | 31·25 — M — 27·00 | 1·58 | 1·59 11° H. ∴ 1·58 15° |
| | Propargyl acetate $C_3H—M—CO_2CH_3$ ... ... | 31·25 — M — 49·71 | 1·007 | 1·005 20° B. 1·003 12° H. |
| | Propargyl alcohol $C_3H—M—OH$ ... ... ... | 31·25 — M — 10·21 | 0·967 | 0·963 21° H. ∴ 0·967 15° |
| | Phenylnitromethane $C_6H_5—M—NO_2$ ... ... | 74·45 — M — 26·74 | 1·165 | 1·160 20°/4 I. ∴ 1·165 15° |
| | Sebacic acid $CO_2H—M_8—CO_2H$ .. ... | 23·80 — $M_8$ — 23·80 | 1·13 | 1·132 Cr. |
| 110 | Brassidic acid $C_2H_3—M_{19}—CO_2H$ .. ... | 41·87 — $M_{19}$ — 23·80 | 0·895 | 0·858 57°/4 Va. ∴ 0·89 15° |
| | Hexachlorpropane $CCl_3—M—CCl_3$ .. ... | 69·74 — M — 69·74 | 1·61 | 1·626 C. |
| | Tetrachlorethane $CCl_3—M—Cl$ ... ... ... | 69·74 — M — 23·01 | 1·539 | 1·530 17° Re 1·576 19° Re |
| | Brommethylchloroform $CCl_3—M—Br$ ... ... ... | 69·74 — M — 27·00 | 1·869 | 1·884 0° H. ∴ 1·863 15° |
| | Trichlorethyl acetate $CCl_3—M—CO_2CH_3$ ... | 69·74 — M — 49·71 | 1·409 | 1·391 23° G.T. ∴ 1·40 15° |
| 115 | Trichlorethyl alcohol $CCl_3—M—OH$ ... ... | 69·74 — M — 10·21 | 1·551 | 1·55 20°·3 G.T. |

(To be continued.)

## THE VALUE OF SCIENTIFIC RESEARCH.*

### *The Wheat Pests Problem.*

IT is now well recognised that scientific research is of great money value, but it is not often that successful practical results follow so quickly upon research as in the recent campaign against the insect pests in the vast quantities of wheat which, owing to the war, accumulated in Australia. In this campaign, South Australia played a very important part. In the early stages of the weevil plague, at the instance of Mr. G. G. Nichols, Manager of the South Australian Wheat Scheme, a Wheat Weevil Committee was appointed, consisting of Dr. W. A. Hargreaves, Director of the South Australian Department of Chemistry (Chairman), Mr. G. G. Nicholls, Mr. W. J. Spafford (Superintendent of Experimental Work, Department of Agriculture), Mr. A. M. Lea (Emtomologist to the S.A. Museum), Mr. E. A. Badcock (Manager, S.A. Farmers' Co-operative Union, Ltd.), and Mr. J. T. Jackett (Miller). Subsequently Mr. D. C. Winterbottom (Supervisor of Weevil Department in S. A. Wheat Scheme) was added to the Committee. The work of scientific research on the subject was taken up by the Department of Chemistry, and from experiments conducted in the laboratory of that Department three practical systems of treatment were devised. These, when put into use by the Wheat Boards in the States of South Australia, Victoria, and Western Australia, resulted in saving wheat worth at least £1,500,000, besides giving very valuable knowledge on the whole problem of stored wheat which will be of service in the future. This estimate of monetary value is an approximation. It is, however, based on the observation that the actual weevil damage was at least reduced to one-half of what it would otherwise have been. Senator Russell, Chairman of the Australian Wheat Board announced on January 10 of this year that the actual weevil damage done to the wheat purchased by the British Government during the time it was held after purchase and before shipment had been assessed at 2,200,000 bushels, and that the British Government had agreed to pay the Australian Wheat Board the sum of £552,000 to cover this loss. This was based on the contract rate of 4s. 9d. per bushel. The amount paid for losses can be taken as a low estimate of the value of the wheat saved for the British Government. During the three years 1915-16, 1916-17, 1917-18, the Commonwealth production of wheat was 404,000,000 bushels, of which South Australia contributed 98,000,000, and Victoria 136,000,000 bushels. The British Government contract was for 112,000,000 bushels, of which South Australia supplied 36,000,000, and Victoria 40,000,000 bushels, so that in round figures the British Government took about one-quarter of the Commonwealth output, and this entailed about one-third of the output of South Australia and Victoria. The savings to each of the States of South Australia and Victoria can be taken then to be at least an equal amount to that saved for the British Government. Hence we arrive at the conservative estimate of £1,500,000 worth of wheat saved from destruction as the result of scientific research. The following figures may help to demonstrate the extent of the undertaking as it affected South Australia, where the wheat had to be safeguarded from mice, weevils, etc The crop carried over from 1917-18 and in stacks was 42,000,000 bushels. The 1918 crop was 26,000,000 bushels, making a total of 68,000,000 bushels on hand. During the twelve months following only about 11,000,000 bushels were disposed of, leaving nearly 57,000,000 bushels to be carried over to 1918-19. The 1919 crop was over 20,000,000 bushels, and left no less than 77,000,000 bushels to be guarded. Some idea of the magnitude of the work can also be gained from the following remarks made by Mr. R. A. Love, who was the Australian Commissioner for the Royal Commission of Food Supplies in London: "The cleaning, sterilising, and handling that had to be undertaken in Australia in connection with the wheat was without doubt the largest campaign of its sort that the world has ever had to undertake When one considers the enormous amount of labour and the handling involved to enable the vast quantities to be cleaned, sterilised, and made fit for shipment, it was truly colossal In looking back over the work, I think we can be proud of the results of our labours. It is nice to feel, considering the enormous amount of thought and worry put into the task, that it was successful in results, efficiency, and cost. The gassing campaign without doubt saved an enormous amount of money, and enabled vast quantities of wheat to be held over until they could be treated." The methods recommended by the Wheat Weevil Committee as the result of the scientific research carried out by the Department of Chemistry were the following.

1. *Cleanliness.*—The weevil was recognised as a pest which was fostered by careless and dirty conditions. Cleanliness in the collection, transport, and storage of the wheat was therefore advocated. In storage, the chief problem was to prevent contamination of the stacks from without. Hence the following precautions were enjoined: absolutely clean stacking sites, impervious insect-proof floors, thorough cleaning up of old stacking sites, and gutters filled with water, oil, or molasses, placed around the base of the stacks to prevent access of crawling weevils. Stacks were either enclosed in hessian and then limewashed, or wherever practicable, entirely enclosed in mathoid sheds. The malthoid sheds, first tried at the suggestion of Mr. A. M. Lea, a member of the Wheat Weevil Committee, proved the most successful.

2. *Gas Treatment.*—The use of poison gas for the extermination of vermin is by no means a new idea, and as far back as 1890, gas plants were used in South Australia for the purpose of suffocating rabbits in their burrows by means of air deprived of its free oxygen by being passed through a fire. During the mouse plague of 1916-17, Dr. Hargreaves had suggested the use of a gas producer plant for providing large quantities of cheap gas for the extermination of mice, and in the middle of 1917, Mr. Saunders, of Clutterbuck Bros., of Adelaide, experimented with producer gas as a means of destroying weevils, but these initial experiments were unsatisfactory because the treatment was not continued nearly long enough. Carbon dioxide compressed in cylinders had been advocated in 1898 by Noel Paton, and

*From "Report No. 2 of the State Advisory Council of Science and Industry of South Australia."

in 1911, 1912, and 1913, by Barnes and Grove, but their methods were prohibitive on account of cost. It was not until the time factor was shown to be an important one, by experiments with weevils in closed bottles, carried out in January, 1918, by Mr. Spafford, a member of the Committee, that gas treatment was found effective. Mr. D. C. Winterbottom, chemist in the Department of Chemistry, was transferred to the South Australian Wheat Scheme as officer supervising weevil destruction, and he installed the first gas plant in Australia. It was a decided success. Subsequently other plants were installed by him in South Australia and Victoria, and similar plants were used in Western Australia. The operation of these gas plants in South Australia was placed in the hands of Messrs. S. D. Shield and E. A. Pengelly, research chemists of the Department of Chemistry, and in Victoria the plants were in charge of Mr. P. J. Thompson, of the Melbourne University. The method employed was as follows. The stacked grain was entirely enclosed in sheds covered with malthoid or similar material made as nearly air-tight as possible. Then air freed from free oxygen by being passed through a furnace similar to that of a gas producer, but producing carbon dioxide instead of carbon monoxide, was blown into the shed for three or four weeks to asphyxiate the insects. Many large stacks were thus successfully treated. In one case the stack contained 200,000 bags of wheat.

3. *Heat Treatment.*—In the cleaning and shipment of the weevilly wheat, heat treatment to a temperature of 140° or 150° Fahrenheit was found to be the most effective method of checking further outbreak of weevil. Soon after research was commenced in August, 1917, Mr. Winterbottom found that this would probably be a successful method, and experiments were made to see the effects of heat treatment on the wheat. It was proved that the flour and bread-making properties were not impaired. A machine was invented in the Department of Chemistry and erected at Port Adelaide, which killed all the insects passed through it without damaging the wheat. This was the first successful heat treatment plant in Australia. Professor Lefroy was working on behalf of the British Commission in Sydney, and he investigated a large number of devices for destroying weevils, including a number of heat treatment machines designed by different inventors. He finally adopted the Poole and Steele machine. At first this machine was not successful, but Dr. Hargreaves was able, as a result of experience gained by the research experiments, to suggest at a conference in Sydney in March, 1918, certain modifications which resulted in the successful working of the machine, which was then adopted by the British Commission. The effects of this successful end to the investigations will be more far-reaching than they appear at first sight. Not only can the saving of the wheat stored during the war, which would otherwise have been destroyed by insect pests, be directly credited to scientific research, but the results obtained have demonstrated the practical value of the methods used. These methods can be used in future, so that the total money value of the research is beyond assessment.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

*Ordinary Meeting, January 27, 1921.*

Prof. C. S. SHERRINGTON, President, in the Chair.

THE following papers were read :—

*"The Myogram of the Flexor-reflex Evoked by a Single Break-shock."* By K. SASSA and Prof. C. S. SHERRINGTON.

In the spinal preparation a single break-shock applied to an afferent nerve or to local skin evokes, when the shock is considerably above threshold value, a reflex contraction which is both stronger and more prolonged than is the maximal twitch evoked from the motor nerve itself. This is so, whether or no the muscle retains its intrinsic proprioceptive reflex arc. This excess of the reflex contraction over maximal twitch indicates that summation of successive contraction-waves is present in the former. Repetitive discharge from the reflex centre occurs therefore in response to a stimulus consisting of a single induction shock. The reflex repetitive response is more ample, strong, and prolonged in the spinal condition than in the decerebrate.

*"'Intertraction' between Albuminous Substances and Saline Solutions."* By Sir ALMROTH WRIGHT.

The paper takes, as its point of departure, the observation that the introduction of 5 per cent salt solutions into wounds is followed by an abundant outflow of albuminous fluid. There is thus provided an agency—an agency largely employed in the war in the treatment of foul wounds—by which corrupted discharges lodged in recesses of a wound can be evacuated and then replaced by uncorrupted fluid drawn from the blood.

It is demonstrated in this paper by means of experiments in which serum is directly superimposed upon heavier salt solutions, and corresponding experiments in which lighter salt solutions are superimposed upon heavier serum, that the fluids thus brought into conjunction interpenetrate with extreme rapidity—the lighter fluid being carried down into the heavier subjacent fluid, while at the same time the heavier fluid is carried up into the superjacent stratum.

The mechanism of this is described and discussed, and it is shown that the phenomena are due to an interaction between the salts and the albuminous substances. The designation "intertraction" is applied to this form of interaction; and it is suggested that these forces supplement diffusion and are an important agency in bringing about interfusion.

In supplementary experiments it is shown that by the aid of the intertraction here in question microbes lodged in serum are rapidly carried down into heavier, or caught up into lighter, salt solutions.

*"Local and Generalised Action of Radium and X-rays upon Tumour Growth."* By S. RUSS, D.Sc., HELEN CHAMBERS, M.D., and GLADWYS M. SCOTT.

The attempt has been made to find the effects of the beta and gamma rays from radium and

X-rays upon rat tumours, under varying conditions. The local effects were obtained by exposing the tumour only to measured quantities of radiation, the animal not sharing, to an appreciable extent, in the irradiation.

When large doses are employed, destructive action upon the tumour cells is observed; as the dose is reduced, the action tends to become stimulative in character, so that the tumour cells grow more rapidly than they would, had they received no radiation.

The generalised effects of the rays used were obtained by submitting the whole animal to the radiation, the tumour in the animal being screened by the use of suitable screens. It was found that large generalised doses could not be borne by the animals; when, however, they were given repeated small doses, an increase in body weight and an increase in resistance towards tumour growth was observed.

Under the usual conditions of radiation treatment in malignant disease in man, the body shares to some extent in the radiation administered to the tumour, and the bearing of the present observations in this connection is discussed.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.*

Vol. clxxi., No. 19. November 8, 1920.

CATALYTIC DEHYDRATION OF AMYLIC ALCOHOL OF FERMENTATION.—M. J. B. Senderens.—It is generally known that amyl alcohol, which boils between 129° and 132° is a mixture of isopropylethyl alcohol and methylethylethyl alcohol. These alcohols dehydrate in the presence of zinc chloride, which is represented by the following accepted equations :—

(a) $\begin{matrix}CH_3\\CH_3\end{matrix}\rangle CH \cdot CH_2 \cdot CH_2OH =$

Isopropylethyl alcohol

$\begin{matrix}CH_3\\CH_3\end{matrix}\rangle CH \cdot CH : CN_2 + N_2O$

Isopropylethylene

(b) $CH_3 \ \begin{matrix}CH_2\\CH_3\end{matrix}\rangle CH \cdot CN_2OH =$

Methylethylethyl alcohol

$\begin{matrix}CH_3 \cdot CH_2\\CH_3\end{matrix}\rangle C : CH_2 + N_2O$

methylethylethylene

In reality the principal product of dehydration of amylic alcohol of fermentation by zinc chloride is trimethylethylene $\left(\begin{matrix}CH_3\\CH_3\end{matrix}\rangle C : CH \cdot CH_3\right)$. According to Wischnegradsky this dehydration should furnish 50 per cent of trimethylethylene, soluble in dilute sulphuric acid (2 vol. of strong acid+1 vol. of water) the insoluble portion consisting of isomeric amylenes and amylene hydrides (*Comptes Rendus*, 1878, lxxxvi., 973; *Bull. Soc. Chim.*, 1877, i., 261 and 452; 1892, ii., 1340). It is the hydrolysis of this sulphuric acid solution of trimethylethylene which gives the hydrate of amylene $\begin{matrix}CH_3\\CH_3\end{matrix}\rangle COH.CH_2.CH_3$ and tertiary amyl alcohol.

Vol. clxxi., No. 20. November 15, 1920.

MICROCHEMICAL REACTIONS OF SODIC ACID.—M. A. Bolland—The following reactions have been obtained using an aqueous solution of solid iodic acid. (1) With thallium nitrate. In the first instance, needles are formed which unite into crosses, simple, double, and multiple. The microscopic appearance is in general similar to the iodide of palladoammonium. Their mean length is about 40 $\mu$ The best strength of solution to use in order to obtain the precipitation is 1 : 5000 (iodic acid . water). (2) With silver nitrate. The product of the reaction is amorphous. It dissolves in ammonia; after evaporating off the ammonia, rhombic plates are obtained, similar to those of manganese oxalate. Strength of solution, 1 : 5000. (3) With barium chloride. Barium chloride precipitates needles. Their length being up to 300$\mu$. Strength of solution, 1 : 2500. (4) With Strontium Acetate. Needles and thin prisms are obtained, their length reaching to 100 $\mu$. Strength of solution, 1 : 300. (5) With calcium acetate. Colourless octahedra are obtained, whose extinction between crossed Nicols show that they belong to the monoclinic system. Mean length, 150$\mu$. Strength of solution, 1 : 300. The author has experimented with many other reagents, including rubidium chloride, ammonia, &c , the results of which he gives in the above paper.

## NOTES.

TOXICITY OF BARIUM CARBONATE TO RATS.—A series of experiments on the toxicity of various substances to rats and their suitablity for poisoning these animals was undertaken by the U.S. Bureau of Chemistry as part of the rat-extermination work of the Department of Agriculture. The results of the tests with barium compounds brought out the following facts. *Lethal Dose for* Rats.—Barium chloride, subcutaneously, 45 to 89 mgrms. per kilo., by stomach tube, 350 to 535 mgrms. per kilo; barium carbonate, per os, 630 to 750 mgrms. per kilo. On the basis of the barium content, the carbonate is about two-thirds as active as the chloride when administered per os. The average intake of food, both poisoned and unpoisoned, by hungry white rats, was one-hundredth of their body weight. 20 per cent of barium carbonate in the rat bait was found to be an efficient concentration. With this percentage a rat is required to eat only one-third or three-eighths of a meal of average size, or 1/320 to 1/266 of its own weight, in order to secure the ingestion of a lethal amount. With this concentration, many of the rats die within the first 24 hours, the chief factor being the consumption of an amount larger than the minimum efficient lethal dose.—*Journal of the Franklin Institute*, January, 1921.

THE USE OF AMMONIUM PERSULPHATE FOR REVEALING THE MACROSTRUCTURE OF IRON AND STEEL (U.S. Bureau of Standards, Scientific Paper No. 402).—Ammonium persulphate is a widely used etching reagent for copper alloys, but the advantages of its use with iron and steel have been almost entirely overlooked. The article describes the method of application of the reagent and gives photographs to illustrate typical results obtained. Ammonium persulphate decomposes upon the ad-

dition of water, so that the action of the reagent is that of a weak acid intensified by the presence of oxygen. Chemical unhomogeneity is readily shown by the reagent, but the most characteristic feature in its action is the readiness with which it reveals the crystalline condition of the material —*Journal of the Franklin Institute,* January, 1921.

"100 PER CENT." *Daily Mail* EFFICIENCY EXHIBITION.—From February 10 to February 26 the *Daily Mail* Efficiency Exhibition will be open at Olympia. Its scope and interest may be measured from the following summary of its main sections Scientific—Research, Invention, Motion Study, Chemistry &c. Industrial—Factory planning, Equipment and Plant, Waste Elimination, Employees' Welfare, &c. Commercial—Organisation, Distribution, Printing, Advertising, Costing, Office Equipment, Insurance, &c Civic and National—Education, Physique, Traffic, Transport, &c. Personal—Technical and Professional Colleges, Mind Training, Vocational Guidance, Languages, &c. An important exhibit will be that illustrating the work of the Ministry of Labour's Industrial Training Department. This Department is responsible for the intensive training of ex-Service men in skilled trades, and the whole of the Olympia Annexe will be devoted to showing how the ex-fighting man is quickly trained to help the nation win in the great Industrial World-War. The Efficiency Exhibition and the lessons to be learned there promise to mark the beginning of a new era for the British man of business, whatever industry or calling he may be associated with. It will be responsible for much "scrapping" of machinery, methods, and buildings. A period of trade depression and low output is the very moment when important reconstruction work can be undetaken. The present slack time offers golden opportunities to those with foresight and imagination, and the *Dail Mail's* Efficiency Exhibition comes at an extraordinarily opportune moment. We are no longer too busy to think, and Olympia in February will *make* us think.

ROYAL INSTITUTION.—A General Meeting of the members was held on the 7th inst., Sir James Crichton-Browne, Treasurer and Vice-President in the Chair. Mr. J. McIlwaine Cater, Mr. C. C. Paterson, and Mr. C. Western were elected members. On Saturday, February 12, at 3 o'clock, Prof. A. Fowler begins a course of three lectures at the Royal Institution on "Spectroscopy." The Friday evening discourse on February 11 will be delivered by Dr F. W. Aston on "Isotopes and Atomic Weights," and on February 18 by Mr. Solomon J. Solomon on 'Strategic Camouflage."

# New Patents.

THIS List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

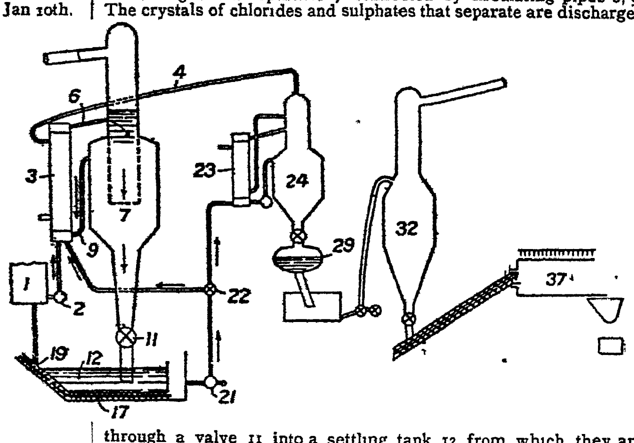
2068—Ashcroft, E. A.—Metallurgy of lead and zinc and their sulphides. Jan. 14th.
1172—Barron, E. C.—Chemical fire-extinguishers. Jan. 10th
1447—Brat, P.—Recovering nitrogen in the form of ammonia from peat. Jan. 10th.
1911—Clavel, R.—Treatment of cellulose acetate or products made therewith. Jan. 12th.
1690—Foster, J.—Method of producing lime for building together with ammonia and a gas for power purposes. Jan. 11th.
1191—Helbronner A.—Manufacture of sulphuric acid. Jan 10th.
1415—Hilpert, S.—Treatment of waste sulphuric acid. Jan. 10th.
1946—Hodge, J.—Sulphuric-acid valves. Jan 13th.
1687—Wailin, E.—Production of steinholz from magnesia and magnesium salts. Jan 10th.
2693—Bader, W.—Manufacture of pyrosulphates. Jan 20th. British Cellulose & Chemical Manufacturing Co., Ltd.
2554—Conover, C.—Purification of naphtalene. Jan. 19th.
2224—Delaroziere, F. F.—Manufacture of sodium and potassium ferro-cyanide. Jan. 17th.
2275—Kestner, P.—Metallic media for fixation of oxygen of water in appartus for abstracting gases from liquids. Jan. 17th.
2589—Lunden, H. L. R.—Production of nitrogen compounds by absorption of nitrogen in a mixture of reaction. Jan. 19th.
2914—Lunden, H. L. R.—Preparation of a mixture of compounds of alkaline earth metals and carbon for absorption of nitrogen. Jan 22nd.
2281—Pearson, A—Manufacture of zinc oxide Jan. 17th.
2412—Wargons Aktiebolag—Method of producing cyanamide from calcium cyanamide. Jan. 18th

*Specifications.*

156069—Steel, B. D. and Robertson, R. B.—Method of conducting fusions with molten caustic soda or caustic potash.
152975—Toniolo, C. and Officine Elettrochimiche Dottor Rossi—Processes for the production of hydrogen and mixtures hydrogen and nitrogen.
145511—Badische Anilin and Soda-Fabrik—Manufacture and production of solutions of cellulose acetates.
147099—Still, C—Method of treating crude gas liquor to obtain ammonia solution
156831—Gee, J. E.—Thermostats.
156892—Wade, H. Manufacture of insoluble of thorium compounds
156896—Howse, G. H.—Solutions of phenol-alde-hyde condensation products.
156916—Manufacture of acetic acid.

*Abstracts.*

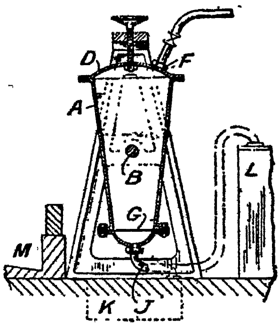
Mr J. B. Hobsbawn of Hove, has obtained a Patent No. 153649 or a new method of obtaining Sodium Nitrate from its solutions. First separate a considerable proportion of the sulphates and chlorides present by concentration under an absolute pressure of 11lb. per square inch until the temperature of 90-95° C, is reached and afterwards concentrating the liquor at atmospheric or other pressure until the content of chloride (calculated as the sodium salt) is 75-80 grams. per litre. The concentrated liquor is then cooled for the production of sodium nitrate crystals. The first stage of the concentration is effected in a vacuum evaporator, consisting of a heater 3 and a separator 7 connected by circulating pipes 6, 9. The crystals of chlorides and sulphates that separate are discharged




through a valve 11 into a settling tank 12 from which they are removed by conveyors 17, 19. The crystals may be washed by liquor from the store tank 1. A pump 2 feeds liquor from the store tank 1 to the heater 3, and a pump 21 returns the liquor from the settling tank 12 to the heater. The second stage of the concentration is effected in an intermittently working evaporator consisting of a heater 23 and a separator 24 operating under a pressure such that the steam generated may be led by a pipe 4 to the heater 3 and

used as a heating-agent therein. The evaporator 23, 24 is filled by adjusting a valve 22 so as to permit a portion of the liquor from the pump 21 to enter the heater 23. When the liquor has reached the prescribed concentration the contents of the evaporator 23, 24 are discharged through a filter 29 and are pumped into a chamber 32 maintained under an absolute pressure of 12-13lb per square inch, and are cooled to 70-75° C by evaporation under the reduced pressure. The liquor is then transferred to a rotary cooler 37, in which the sodium nitrate separates.

*Ammonium Sulphates*—A new process for treating Ammonium Sulphates is the subject of a Patent No. 154328 by Mr N Wilton of 100, Station Road, Hendon. To remove mother liquor from wet sulphate of ammonia the crystals are placed on a perforated plate G within a vessel A provided with a cover D, and dry steam or steam and air is blown in from the top by pipe F in order to drive the liquid out by a pipe J to the saturator L or to the tank K. Ammonia may be introduced at any stage to neutralise remaining acid. The vessel A, which may be steam jacketed and made of acid resisting material, is mounted on trunnions B to allow of the dried crystals being tipped out into the storage chamber M.




Messrs. Rayner & Co., will obtain printed copies of the published specifications and forward on post free for the official price of 1/- each.

## MEETINGS FOR THE WEEK.

*Monday, February 14.*

Royal Society of Arts, 8. (Cantor Lectures). "Applications of Catalysis to Industrial Chemistry," by Dr. Eric K Rideal
Institution of Electrical Engineers, 7. Discussion on Design of a Large Power Station." Also Meeting at Newcastle, 7.15—"Temperature Units of Large Alternators," by G A Juhlin
Biochemical Society.

*Tuesday, February 15*

Royal Institution, 3. "The British Soldier since the Restoration—His Unmilitary Services," by Hon J. W. Fortescue
Society of Chemical Industry, (At Edinburgh)
Institution of Petroleum Technologists, 5.30

*Wednesday, February 16.*

Royal Society of Arts, 4.30.
Royal Microscopical Society, 8.

*Thursday, February 17.*

Royal Institution, 3. "Oceanography—The Sea Fisheries" by W. A. Herdman.
Institution of Electrical Engineers, 6. "Feebly Magnetic Materials" I—"Instrumentation" by Prof. E. Wilson.
Institution of Mining and Metallurgy, 5.30
Chemical Society, 8.
Royal Society. "A Comparison of Magnetic Declination Changes at British Observatories," by Dr. C. Chree. "The Transmission of Electric Waves round the Earth's Surface," by Prof H. M. Macdonald. "The Stability of Fluid Motion," by Prof. T. H. Havelock. "On the Transformation of Integrals," by Prof. W. H. Young. "The Constitution of the Alloys of Aluminium, Copper and Zinc, containing High Percentages of Zinc," by J. L. Haughton and Kathleen E. Bingham.

*Friday, February 18.*

Royal Institution, 9. "Strategic Camouflage," by Solomon J. Solomon.
Royal Society of Arts, 4.30.
Institute of Metals, 7.30. (At Sheffield).

*Saturday, February 19.*

Royal Institution, 3. "Spectroscopy—Regularity in Spectra," by A. Fowler.

## NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemical Apparatus, &c, for review or notice to be addressed to the EDITOR.

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THE CHEMICAL NEWS.

VOL. CXXII, No. 3175.

## THE UTILISATION OF BASIC SLAG.

By E. J. RUSSELL, D Sc., F.R S., Director of the Rothamsted Experimental Station.

THE utilisation of basic slag in agriculture is one of those important developments in agricultural science for which the credit is due in the first instance to British investigators. The possiblity of utilising basic slag was put to practical test by the late John Wrightson at Ferryhill and at Downton in 1884 and 1885, and, in spite of some opposition on theoretical grounds by other workers, a good case was made out. The first field experiments were carried out in the south of England, but the centre of interest soon shifted to the north, and the most striking tests were carried out at Cockle Park, under the direction successively of Prof. Somerville, Sir. T. H. Middleton, and Prof. Gilchrist. To these three more than any others we owe the great advances in knowledge of the use of basic slag.

The standard experiments and the well-known trials were all made with the Bessemer slag. If agriculturists could have been assured of a steady supply of, say, 300,000 or 400,000 tons per annum of high-grade Bessemer slag containing some 20 per cent of $P_2O_5$, there would have been no need for this discussion; the problem would have been the purely academic one of working out the constitution of the effective constituents of the slag.

The introduction of the basic open hearth process, however, has threatened the supersession of the Bessemer process, and agriculturists can no longer feel certain of receiving adequate supplies of slag of the type to which the old material belonged. Three distinct substances are now used under the one name of basic slag :—

(1) Bessemer slag, containing about 20 per cent $P_2O_5$ (43·6 per cent tricalcic phosphate).
(2) Open hearth basic slag, 7 to 14 per cent $P_2O_5$ (15·4 to 31 per cent tricalcic phosphate).
(3) Open hearth basic slag, 7 to 10 per cent $P_2O_5$ (15·4 to 21·8 per cent tricalcic phosphate), in the manufacture of which a considerable proportion of calcium fluoride has been used.

The phosphorus of the first two types of slag is nearly all soluble (85 per cent or more) in 2 per cent citric acid under certain conventional conditions: that of the third type is not—only 20 per cent or less dissolving.

It may be said at once that no important agricultural distinction between the first and second of these classes has been proved with certainty when the slags are used in quantities containing equal amounts of phosphorus, and so far as present information goes, these slags are of equal value per unit of phosphorus to agriculturists. There are, of course, disadvantages in low-grade materials, in that large bulks have to be handled, and therefore larger expenditure is incurred, and deliveries to the form or field may be delayed. But when allowance has been made for these items, there is no great difference between the two classes of slag. The third class, however, is somewhat different, and agricultural investigators generally agree that it is less effective than the first two types, though they have not yet wholly succeeded in evaluating it.

Broadly speaking, the problem resolves itself into three broad divisions :—

(1) What is the agricultural value of the various basic slags likely to be available in the near future?
(2) Is this value related to the chemical constitution of the slag in any simple way that would allow of some chemical expression and on which an evaluation method might be based?
(3) Is it possible for the steel works to increase the phosphorus content of the slag and generally to increase the effectiveness of the so-called low-grade slags?

The determination of agricultural value requires in general two distinct types of experiments —pot experiments and field trials. Pot experiments are more accurate than field trials, being much more under control: results can be obtained in a single season which are reliable within about 5 per cent. On the other hand, the rigid control of the conditions introduces a large element of artificiality, so that the results are never final. In the writer's experience, a positive result in pot experiments is not always paralleled by a positive result in the field, as some nullifying factor may come into operation; on the other hand, a negative result in pot experiments is usually associated with a negative result in the field.

Although the pot experiment gives useful information, the field experiment has always to be made before any idea can be formed as to the economic importance of the factor under investigation. It is necessary also that the field trial should be repeated on different types of soil and in different climatic conditions. Fortunately, an organisation of agricultural investigators—the Agricultural Education Association—covers Great Britain, and enables co-operative trials to be made. An extended trial of the three types of basic slag is now being organised which should give much valuable information.

The difficulty of studying this particular problem in the past has been to obtain basic slag of known history. In one or two instances a long, laborious agricultural investigation has been deprived of much of its value because the slag supplied for the purpose was not what had been promised.

Field experiments when well carried out are liable to an error of about 10 per cent. Farmers' trials are less reliable: the error may be anything from 20 to 100 per cent, or even more.

Provided the supply of basic slag of known origin can be assured, the agricultural trials can be carried out by the sub-committee of the Agricultural Educational Association, which has been set up for this purpose.

So much for the method of investigation. We must now consider some of the general results. The old Bessemer slag has proved in the farmers' experience extraordinarily valuable for the improvement of heavy grassland; no single fertiliser has been anything like as effective for this particular purpose. The effect is mainly indirect, and is traceable to the remarkable development

of white clover which follows the application of the slag. It is not yet ascertained whether this effect is due to direct action of phosphates on the plant, or whether the slag in some way is helpful to the micro-organisms associated with the clover root.

Whatever the cause, the result of this spread of white clover is to increase the stock of nitrogen in the soil, and add greatly to the soil fertility. Further, it adds considerably to the value of the herbage, clover being one of the best of the green foods available. Another factor also contributes to the nutritive effect; additions of phosphate to the soil tend to add to the phosphorus content of the crop, and this in turn raises its feeding value

The use of Bessemer basic slag has not been restricted, however, to grassland. It has proved effective in increasing yields of crops on arable land, particularly in the West and North. So far as the evidence goes, the feeding value of the crop is also increased, though the experiments are not very numerous.

As already stated, the open hearth basic slag made without fluorspar has hitherto proved practically as effective as the old Bessemer slag when compared on the basis of equal amounts of phosphorus. The fluorspar slag, has, however, proved distinctly less effective in pot experiments and in Oldershaw's field experiments in Suffolk; it was also less effective (though quite good) in some of Robertson's field experiments in Essex. In the North and West, however, where the growing season is longer, it was nearly as good as the more soluble slag of the second type. We may infer that the fluorspar slag would probably be more effective in cool, moist regions than in hot, dry ones, though more information is needed before a definite rule could be made.

The chemical or physico-chemical problem of elucidating the constitution of basic slag and determining the effective components is more difficult.

It has always been assumed that the phosphate was the effective constituent, this being the only one of the three common fertilising constituents—nitrogen, phosphorus, and potassium—present. Some importance used to be attached to the free lime until it was realised that not more than 2 to 5 per cent of free lime is present, so that the amount added to the ground is negligible. The Bessemer slag, however, produced effects on heavy grassland which could not be obtained by equivalent dressings of mineral phosphate or superphosphate. It is necessary to find some explanation for this result, and usually in Great Britain it is assumed that the phosphorus in basic slag is in the form of a silico-phosphate which may be assumed to differ in physiological action from the ordinary phosphate. Hall and Morrison (*Proc. Roy. Soc.*, 1909, 77B, 455-477) have shown that silica affects the intake of phosphorus by the plant; and the increased assimilation they obtained when silica was added to phosphate may offer an explanation of the efficacy of basic slag on grassland.

In France, on the other hand, considerable attention has been devoted to other constituents besides nitrogen, phosphorus, and potassium. Mazé (*Annales Inst. Pasteur*, 1919, xxxiii., 139-173) maintains that a large number of elements, in addition to those ordinarily recognised, including boron, aluminium, fluorine, iodine, chlorine, silicon, manganese, and zinc, are necessary for the full growth of the plant. Other workers have experimented with some of these as fertilisers, and have shown that manganese (W. E. Brenchley, *Ann. Bot.*, 1910, xxiv, 571-583; E. P. Dearrick, Cornell Univ Ag. Mem., 1919, xix, 371-402; J. S. McHague, *Journ. Ind. Eng. Chem.*, 1919, xi., 332-5) and fluorine (A. Gautier and P. Clausmann, *Compt. Rend.*, 1910, clxviii., 976) compounds may give increases in crop From the published details in the French papers it is not evident that such increases would usually be obtained in the field, but in so far as they are obtainable at all in soil, they indicate that other constituents of slag besides phosphorus are effective. Indeed, the manganese content of slags is actually determined in France.

The experiments made in England with manganese compounds as fertilisers have not led to promising results. At Rothamsted, manganese dioxide and manganese sulphate were both tried, both succeeded to a small extent in pots, but failed in the field. At Woburn, also, some degree of success was obtained in the pot experiments. We do not, however, know of a single case in this country where manganese salts have given unexceptionable increases in crop in the field. It may always happen, however, that other compounds would be more effective, and we have started in the pot culture house a series of experiments with slags of known manganese content in order to ascertain whether manganese in the form in which it occurs in slag behaves in any way differently from the oxide or sulphate.

The idea has been put forward (probably by some of the slag grinders) that the composition of basic slag is less important than the state of grinding. It is true, of course, that a certain degree of fineness is necessary in order that the slag may have some chance of acting; Collins (Collins, "Plant Products and Chemical Fertilisers," 1918) has adduced some evidence that the standard sieve of 100 meshes to the inch affords the best results; more extended experiments, however, might well be made. But there is no evidence whatsoever for supposing that fineness of grinding is the sole factor or is anything more than an important secondary consideration It has been asserted that a 20 per cent slag finely ground would have exactly the same effect as an equal weight of 30 per cent slag finely ground, and therefore that the low-grade slag ought to find just as ready a market as the higher grade slag. Hitherto the claim has not been taken sufficiently seriously to justify any special investigation, and the direct experiments have always been with quantities of slag containing the same amount of phosphorus.

There is, however, no indirect evidence even remotely suggesting that the addition of 5 to 10cwt. per acre of a mere gritty substance would have any appreciable effect on the soil. Many attempts have been made in the past to improve clay soils by the addition of sand; they broke down because the amounts needed per acre were not a few cwts., but many tons. The alteration of soil texture by addition of inert particles is very difficult, necessitating large amount of material.

Reviewing all the evidence, I see no reason to depart from the customary British method of regarding the phosphorus as the essential fetilising constituent in basic slag, though I am prepared to admit that a silico-phosphate might have a special fertiliser value, and that the basic nature of the slag is also important; as to the manganese, I have an open mind, and we are starting a series of experiments at Rothamsted on this problem.

Assuming phosphorus to be the essential fertiliser constituent, it is by no means easy to discover the form in which the phosphate exists in the different slags, or even to solve the purely analytical problem of devising a method which shall discriminate between one slag and another. In the early days there were attempts in Germany to mix cheap mineral phosphate with basic slag and to sell the mixture as a genuine article. The late Prof. Wagner then devised his well-known citric acid test for basic slag, which has become the standard method in most countries ever since. But, as Mr. Scott Robertson has shown, it does not help much for the evaluation of the new kinds of slag, and a new method seems called for.

Perhaps the most pressing problem, however, is the enrichment of basic slags poor in phosphate. In the case of the Bessemer slag this problem does not arise, because it is to the steel maker's interest to have a pig iron rich in phosphorus, and hence the slag is necessarily rich. But in the basic open hearth richness in phosphorus is not essential; indeed, it is not even desirable, and the steel maker takes no steps to ensure a phosphatic pig iron. When it is suggested that the phosphorus content of the pig iron might be increased deliberately with a view to improving the slag, the steel maker points to the relative prices of steel and slag, and reminds one that the tail must not be allowed to wag the dog. Agriculturists must remember that basic slag is a very subsidiary part of the steel maker's business, and that it cannot for a moment be allowed to increase the time necessary for making the steel, nor in any other way to increase greatly the cost of working.

On the other hand, the steel maker should realise that the agricultural demand for good basic slag is likely to be greater than the supply. The consumption of basic slag has greatly increased during the war, and there is no sign yet that the limit has been reached The figures for the consumption in the United Kingdom are, in tons per annum :—

| Pre-War | Year ending May 31st, 1918. | 1919. |
|---|---|---|
| 263,000 | 500,000 | 540,000 |

| Estimated amount utilisable | |
|---|---|
| Sir T. H. Middleton. | Sir Chas Fielding |
| 892,000 | 1,463,000 |

It would be interesting to know from the steel makers what amount of slag calculated in terms of a slag containing 20 per cent $P_2O_5$ is likely to be producible in the near future. There are two distinct cases where enrichment would be desirable :—

(1) Slags containing less than 8 per cent $P_2O_5$ which at present are hardly used; by enrichment these might become worth grinding.

(2) Slags containig 8 to 12 per cent $P_2O_5$ (*i.e.*, 17·4-26 per cent tricalcic phosphate), which are already easily saleable, but which when sold on the basis of $P_2O_5$ content cost a disproportionately large amount in bagging, grinding, and freight.

Assuming enrichment of the pig iron to be out of the question, the only two possibilities seem to be .—

(1) Fractionation of the slag so as to concentrate the phosphorus as much as possible in one part of the slag.

This gives a product which can be more profitably handled by all concerned, though it does not increase, but rather diminishes, the total phosphorus supply.

(2) Enrichment of the slag by adding finely ground mineral phosphate in the ladle.

We are not yet in a position to pronounce a final opinion on this latter method. In its favour may be urged the fact that mineral phosphates have distinct fertiliser value, which is apparently increased by ignition, and might well be increased by any interaction taking place in the ladle.

Against it is the difficulty of detecting fraudulent additions of mineral phosphates to slag, which might become common if there were any great difference in unit price between slag phosphate and mineral phosphate—and without some difference there would be little inducement to the steel maker to enrich his slag.

A further and perhaps more difficult problem is to improve the fluorspar slags, which at present are much less soluble in citric acid than those made without additions of fluorspar. Although these insoluble slags have a higher fertiliser value than was anticipated from the old citric acid test, they do not appear to be as effective as the more soluble ones. Not only is there a falling off in yield, but probably also in quality of the crop Pot experiments indicate that the plant takes up less phosphoric acid from an insoluble fluorspar than from a more soluble one; agricultural experience shows that increased assimilation of phosphoric acid increases the value of the crop as animal and probably as human food

Sould it be impracticable to improve the fluorspar slags, there is still another possible solution. Agriculturists could no doubt find the precise soil and climatic conditions under which they would prove most effective, and efforts could then be made to confine their use to those particular cases.
—*Transactions of the Faraday Society*, December, 1920.

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VARIATIONS IN THE CONDUCTIVITY OF CALCIUM SULPHIDE DUE TO CHANGES OF TEMPERATURE.—When a thin layer of calcium sulphide is heated, previously insolated, its conductivity rapidly increases, passes a very acute maximum, and then decreases to become practically nil. The gradient conductivity-temperature is so much greater, the maximum so much higher, according to the greater rapidity of heating. The phenomenon is really associated with the state of phosphorescence, for when cooling is made before conductivity falls to zero, and then heating, we have much slighter variations and a much smaller maximum. M. Vaillant, who studied this phenomenon summarises his observations in this note.—*Comptes Rendus*, December 27, 1920.

# THE RELATIVE VOLUMES OF THE CHEMICAL ELEMENTS.

By HAWKSWORTH COLLINS. (Continued from p. 66).

In the following the same results are obtained as in the foregoing, but without any intervening $CH_2$.

| | Name and Chem. Formula. | Vols of Parts. | Theor. S.G. | Observed S.G. |
|---|---|---|---|---|
| | Chlorbenzene $C_6H_5$—Cl | 77·48 — 23·01 | 1·119 | 1·126 20° So. 1·107 20° B. |
| | Brombenzene $C_6H_5$—Br | 77·48 — 27·00 | 1·493 | 1·492 22°/4 I. 1·491 20° B. |
| | Iodobenzene $C_6H_5$—I | 77·48 — 32·75 | 1·851 | 1·858 0° Sh. |
| | Nitrobenzene $C_6H_5$—$NO_2$ | 77·48 — 26·74 | 1·180 | 1·187 14° Ko. 1·174 25° Sch |
| 120 | Nitrobenzene $C_6H_5$—$NO_2$ | 74·45 — 26·74 | 1·216 | 1·216 5° — 10° Re. |
| | Aniline $C_6H_5$—$NH_2$ | 74·45 — 16·42 | 1·023 | 1·023 17°/4 Sw. |
| | Benzonitril $C_6H_5$—CN | 77·48 — 23·96 | 1·015 | 1·010 15° Va. 1·024 25° K. |
| | Triazobenzene $C_6H_5$—$N_3$ | $\binom{77\cdot48}{74\cdot45}$— 32·63 | 1·096 | 1·098 10° Va. 1·097 10° P. |
| | Phenyl mercaptan $C_6H_5$—SH | 77·48 — 25·48 | 1·07 | 1·078 14° V. |
| 125 | Thiophenol $C_6H_5$—SH | $\binom{77\cdot48}{74\cdot45}$— 25·48 | 1·084 | 1·074 23° Ei. ∴ 1·081 15° |
| | Benzoic acid $C_6H_5$—$CO_2H$ | 77·48 — 23·80 | 1·205 | 1·201 21° M. |
| | Benzoic acid $C_6H_5$—$CO_2H$ | 74·45 — 23·80 | 1·242 | 1·227 27° M. ∴ 1·24 15° |
| | Phenyl acetate $C_6H_5$—$CO_2CH_3$ | 77·48 — 49·71 | 1·07 | 1·074 Bo. |
| | Phenyl acetate $C_6H_5$—$CO_2CH_3$ | $\binom{77\cdot48}{74\cdot45}$— 49·71 | 1·082 | 1·080 15°/15 Va. |
| 130 | Et. benzoate $C_6H_5$—$CO_2C_2H_5$ | 77·48 — 66·13 | 1·045 | 1·047 20° B. 1·049 14° De. |
| | Ethyl benzoate $C_6H_5$—$CO_2C_2H_5$ | 74·45 — 66·13 | 1·067 | 1·06 18° De. |
| | Propyl benzoate $C_6H_5$—$CO_2C_3H_7$ | 77·48 — 82·55 | 1·0248 | 1·0248 15° Sm. |
| | Butyl benzoate $C_6H_5$—$CO_2C_4H_9$ | 77·48 — 98·97 | 1·009 | 1·011 15° Va. 1·000 20° L. |
| | Amyl benzoate $C_6H_5$—$CO_2C_5H_{11}$ | 77·48 — 115·39 | 0·996 | 0·992 15° Sm. 1·002 10° Dh |
| 135 | Phenol $C_6H_5$—OH | 74·45 — 13·29 | 1·071 | 1·070 20° B. |
| | Phenylacetylene $C_6H_5$—$C_2H$ | 77·48 — 31·25 | 0·938 | 0·937 12° Va. 0·932 25° I. |
| | Bromethylene (Vinyl Br) $C_2H_3$—Br | 41·87 — 27·00 | 1·539 | 1·529 11° A. 1·566 4° Car |
| | Iodethylene (Vinyl I) $C_2H_3$—I | 41·87 — 32·75 | 2·064 | 2·09 0° Gu. ∴ 2·064 15° |
| | Oxalic acid $CO_2H$—$CO_2H$ | 23·80 — 23·80 | 1·9 | 1·900 I. |
| 140 | Methyl ethyl oxalate $CH_3CO_2$—$CO_2C_2H_5$ | 49·71 — 66·13 | 1·14 | 1·156 0° Wi. ∴ 1·142 15° |
| | Hexchlorethane $CCl_3$—$CCl_3$ | 69·74 — 69·74 | 1·70 | 1·619 Re. 2·011 S |
| | Bromotrichlormethane $CCl_3$—Br | 69·74 — 27·00 | 2·041 | 2·058 0° Pt. ∴ 2·04 15° |
| | Methyl trichloracetate $CCl_3$—$CO_2CH_3$ | 69·74 — 49·71 | 1·486 | 1·489 19° H. |
| | Acetylene dichloride $C_2H_2$—$Cl_2$ | 28·89 — $(23\cdot01)_2$ | 1·295 | 1·291 15°/4 Ch. |
| 145 | Acetylene dibromide $C_2H_2$—$Br_2$ | 28·89 — $(27\cdot00)_2$ | 2·22 | 2·223 19° Sb. |
| | Acetylene iodide $C_2H_2$—$I_2$ | 28·89 — $(32\cdot75)_2$ | 2·966 | 3·303 21° Sb. 2·942 21° Sb. |
| | Acetylene chlorobromide $C_2H_2$—ClBr | 28·89 — $\binom{23\cdot01}{27\cdot00}$ | 1·781 | 1·816 0° Pl. 1·747 19° Sb |
| | Acetylene chloriodide $C_2H_2$—ClI | 28·89 — $\binom{23\cdot01}{32\cdot75}$ | 2·227 | 2·229 Pl. |
| | Acetylene bromiodide $C_2H_2$—BrI | 28·89 — $\binom{27\cdot00}{32\cdot75}$ | 2·62 | 2·627 17° Pl. |

In the preceding 149 molecules it will be noticed that there are two of each of the following, -ß phenylethylamine (Nos. 42, 44), benzyl acetate (Nos. 56, 57), nitrobenzene (Nos. 119, 120), benzoic acid (Nos. 126, 127), ethyl benzoate (Nos. 130, 131). The fact that there are two is not a fault of the theory; but, if there is a fault anywhere, it is in the large variations of specific gravity obtained by experimentalists. The *raison d'être* of these variations will appear later. It is only necessary to state here that similar variations occur in nearly all compounds of benzene If this statement contains an actual truth, then, of course, the majority of benzene compounds will be likely to be mixtures of the two forms. This is the explanation of benzyl iodide (No. 39) being given as $\left(\begin{smallmatrix}77{\cdot}48\\74{\cdot}45\end{smallmatrix}\right)$—16·42—32·75. The same remark applies to several others of the foregoing compounds of benzene.

With regard to the two volumes found for OH, nothing can be said at present, except that the distinction between them will appear later.

In No 53, 49·71 is the relative volume of O—CO—$CH_3$, whilst in No. 54 the same figures represent the volume of CO—O—$CH_3$; so that the volumes of these two different arrangements of atoms are the same. The same is true of 66·13 and 82·55.

49·71, 66·13, 82·55, 98·97, and 115·39 are volumes of groups which differ by $CH_2$, and therefore the difference between any two of them ought to be 16·42 or a multiple of 16·42, as it is.

It has been found necessary to begin by investigating the volumes of groups of elements, but later the relative volume of each atom in these groups will become evident.

There is already no doubt at all that perfect regularity exists at the temperature of 15° C , and it remains to be seen how much further this regularity goes, and to what conclusions it leads us.

(To be continued.)

## NOTE ON AUGITE FROM VESUVIUS AND ETNA.

By HENRY S. WASHINGTON and H. E. MERWIN.

THE problem of the constitution of the pyroxenes that contain alumina and ferric oxide—the augites —is one of the most puzzling and, in some respects, one of the most important that are presented by the rock-forming minerals. In an effort to aid its solution, I have made during the last few years a number of analyses of typical augites from Italian volcanoes, in the lavas of which augite is one of the most constant and most characteristic minerals. The study of these is not yet complete, and several more analyses remain to be made. But having recently completed two analyses of augite from Vesuvius and Etna, of which Dr. H. E. Merwin has determined the optical and crystallographic data, it seems to be advisable to publish the results as a slight contribution toward our knowledge of this important group of minerals. This seems to be the more justified as, notwithstanding that the species was based first on the crystals from these two volcanoes, we have as yet no satisfactory or modern analyses of them.

### *Augite from Vesuvius.*

Vesuvius has long been noted for its pyroxenes. Beautiful diopsides are found in many of the ejected blocks of Somma, and loose crystals of augite are among the products of many of its eruptions. The crystals studied here were obtained from the bottom of the crater, in part by me in June, 1914, and in part by Dr. A. Malladra, Director of the Osservatorio Vesuviano, during the same spring. For his kindness in sending me the material for study I would express my sincere thanks.

*Occurrence.*—The crystals are found, either loose, and entirely or almost entirely free of scoria, as at many other volcanoes; or as phenocrysts in a highly vesicular leucite tephrite, which was being ejected in small amount from the orifice at the bottom of the funnel during my visit to it (A. Malladra, *Rend. Acad. Sci. Napoli*, Nov., 1914; Washington and Day, *Bull Geol. Soc. Amer.*, 1915, xxvi., 375).

The crystals are mostly of the usual, well-known, simple forms, such as are figured by Dana ("System", 1892, p. 354, Figs. 16,17,18) and in most text-books of mineralogy. The faces present are: $a(100)$, $b(010)$, $m(110)$, and $s(\bar{1}11)$. A small proportion are twinned, forming the common contact twins, with twinning plane $a(100)$. They vary, in general, from 3 to 5 mm. in length (parallel to the vertical axis), though some attain lengths of 1 cm. or more. The thickness is from one-half to two-thirds of the length, and there is usually a slight tabular development parallel to $a(100)$ The faces are fairly smooth and bright, much brighter than those of the Stromboli augites described in a previous paper (Kozu and Washington, *Amer. Jour. Sci.*, 1918, xlv., 463), and the edges are sharp. There is but little scoria adherent to the loose crystals, but microscopical examination of the powdered material revealed the presence of small amounts of inclusions of glass and crystalline matter (magnetic, leucite, and feldspar).

*Physical Data.*—Of a dozen crystals studied, four had sets of faces that were sufficiently good for approximate measurements (by Merwin). These indicate the probability that crystallographically diopside does not represent augite. The measurements were as follows:—

$m \wedge \bar{m}$ (110) $\wedge$ ($1\bar{1}0$) = 92°0′-93°57′; mean = 92°56′ 4 measurements.

$s \wedge \bar{s}$ ($\bar{1}11$) $\wedge$ ($\bar{1}\bar{1}1$) = 61°20′-59°50′; mean = 60°36′ 8 measurements.

For diopside the measurements are:—

$m \wedge \bar{m} = 92°50′$, $s \wedge \bar{s} = 59°11′$.

Measurements of $\phi$ and $\rho$ four pyramid faces, $s$, gave values of 24°23′-25°5′ and 34°1′-33°15′, respectively, as compared with 25°7′ and 33°4′ for diopside

Speaking of the pyroxenes as a group, Dana (Dana, "System," 1892, 363) long ago pointed out: "It is noteworthy that the angles vary but little even for a wide variation in composition." While this is quite true, yet since that time, with more exact means of measurements and of chemical analysis, a more systematic study of the relations of the physical and chemical properties, and for other reasons, we are beginning to appreciate more than we did thirty years ago the probable importance of even small variations.

An optical examination showed that the Vesuvius augites studied are variable in composition The general colour is a slightly yellowish grey, and there is little indication of zonal structure. There is little if any pleochroism. The index $\beta$ varies from 1·700 to 1·711. The extinction angle is large, as usual, about 45°, but no exact measurements were made, because of the variability in composition and the consequent indeterminateness of the data.

The specific gravity of the crystal fragments used for the analysis was found to be 3·242 referred to water at 23°. This low result is probably to be ascribed to the presence of the glass inclusions.

*Chemical composition.*—For my analysis some of the cleanest loose crystals were selected, and, in order to obtain sufficient material, to these were added crystals obtained from specimens of the scoria from about the orifice. Great care was taken to free the crystal fragments from adherent scoria, and the analysis was made on what was probably as pure material as could be obtained from this source. It was, however, not practicable to obtain material entirely free from the small inclusions of glass, &c., and the analysis, therefore, does not represent an entirely pure augite substance. In spite of this defect, however, it is thought best to publish it, as a slight contribution to our knowledge of the Vesuvian augites, and as illustrative of the dangers, in the form of included foreign matter, that may lurk in the chemical study of many minerals. The presence of the inclusions is also of interest in view of the very close correspondence in chemical composition between these augites and a pyroxenite published by Lacroix, to be mentioned later.

TABLE I.

*Analysis of Augites of Vesuvius.*

| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| $SiO_2$ | 47·60 | 46·95 | 46·42 | 47·90 |
| $Al_2O_3$ | 6·01 | 6·75 | 9·14 | 6·58 |
| $Fe_2O$ | 3·17 | 4·47 | 5·03 | 1·52 |
| FeO | 4·59 | 4·09 | 4 87 | 3·33 |
| MgO | 14·43 | 16·04 | 13·19 | 14·20 |
| CaO | 21·52 | 19 02 | 20·86 | 22·51 |
| $Na_2O$ | 0·70 | n.d. | n.d. | 1·14 |
| $K_2O$ | 0·76 | n.d. | n.d. | 0·38 |
| $H_2O+$ | 0·08 | n d | n.d. | 0·62 |
| $TiO_2$ | 1·52 | n.d. | n.d. | 1·49 |
| $P_2O_5$ | n.d. | n.d. | n.d. | 0·70 |
| MnO | 0·13 | n.d | 0·14 | n.d. |
| SrO | none | n.d. | n.d. | n.d. |
| | 100·51 | 100·32 | 99·65 | 100·39* |

* Including F = 0·02.

1. Augite, Crater of Vesuvius, June, 1914. Washington analyst.
2. Augite, Monte Somma. Doelter analyst. Tschermak's "Min Petr. Mitth", 1877, 283.
3. Augite, Vesuvius. Casoria, ref. *Zs. Kryst.*, 1907, xlii., 881.
4. Pyroxenite, Monte Somma. Pisani analyst. Lacroix, *C R.* 1917, clxv, 209.

*Earlier Analyses.*—The earlier analyses of Vesuvian augites, collected by Dana, Hintze, and Doelter, and most completely by Zambonini (F. Zambonini, "Mineralogia Vesuviana, 1910, 151), very unsatisfactory, either because of their early dates, or because of their incompleteness. However, two of them, which seem to be somewhat less inferior than the others, are given in Table I. While these older analyses show the general characters of augite, yet they all are seriously defective in that titanium dioxide and the alkalies are not determined in any of them, although it is clear from my analysis, and from our knowledge of augites elsewhere, that these constituents are present in distinctly appreciable amounts. The high alumina shown by them is due to the presence of titanium dioxide. Furthermore, the iron oxides are not separated in many of them. Lacroix has called attention (A. Lacroix, C. R., 1917, clxv., 211) to these serious defects in all the existing analyses of pyroxenes of Vesuvius, and I can only join with him in urging the need for better analyses of this mineral group from Vesuvius and from other localities, and incidentally, call attention to the general inferiority of the great majority of the analyses of pyroxenes, especially as regards the fundamental points of selection of pure material, and accuracy and completeness of the analyses.

The publication of analyses of such inferior quality is to be deplored, as leading possibly to seriously incorrect generalisations at the hands of those who accept blindly and without critical judgment any analysis that is offered them. One of the striking features in the study of the chemistry of minerals and rocks is the complacency with which such inferior work is accepted and published. Much of it is based on impure material, often not ascertainedly so, carried out by inexperienced analysts, by poor methods, or with impure reagents; and yet it is accepted in good faith by both analyst and author. This state of affairs has done much—much more than is generally thought—to hinder the progress of our knowledge of the chemistry of minerals.

*Comparison with pyroxenite.*—It is not necessary here to discuss my analysis of the Vesuvius augite, partly because of its being based on impure material, and partly because it will be discussed later, when the series of Italian augites is more nearly complete. Attention must, however, be called to the very remarkable correspondence between it and an analysis by Pisani of a pyroxenite of Monte Somma, published by Lacroix, which is given in column 4 of Table I. Lacroix does not describe this rock in detail, but it would appear to be holocrystalline and composed almost entirely of pyroxene. It is a somewhat noteworthy example of the possibility of diverse crystallisation of a part of a magma, either as a monomineralic or almost monomineralic, granular rock, or as well-formed crystals of a definite mineral.

Lacroix mentions and gives analyses of several types of the pyroxenite, all of which are more or less closely related chemically. It occurs, according to him (A. Lacroix, *C. R.* 1917, clxv., 205), as homoeogenic rocks, that is, "granular forms, not only of the flows, but also of the differentiated portions of the same magma which have not necessarily reached the surface." Such homoeogenic rocks are assumedly of abyssal origin, and, if the general theories of gravitative adjustment of Daly and Bowen are correct, they would be expected to have come up, or been carried up, as broken-off blocks, from very deep down in the volcanic mass My augite crystals, on the other hand, occur, as has been said, in the light scorias that form the uppermost scum or froth of the ascending magma.

This would indicate that, in this case at least, separation by gravity has not been carried to completeness. That this is also true elsewhere is indicated by the occurrence of such augite crystals (almost always of the same crystal form) at other volcanoes, such as Stromboli, Etna, and the Alban volcano. Indeed, they are rather common at many volcanoes, and similarly crystals of cossyrite and kaersutite (sodic hornblende) are met with as such loose crystals at Panelleria and Linosa, to speak only of Italian volcanoes.

But the incompleteness of such a separative process is not to be wondered at, considering the convection currents in, and the presumably violent movements of, the upward-welling mass of magma, as well as the presence of gas, whose bubbles would act like those in a glass of champagne to keep up a dry raisin, which would otherwise sink ("*Forsan et haec olim meminisse juvabit*").

The interesting point is that, with portions of the magma of almost identical composition, we get, in the one case, a typically granular rock, and in the other, well-formed, loose crystals. We have, unfortunately, no detailed petrographical description of Lacroix's pyroxenites Of some of them he says (p. 210) that they are composed of "a little leucite filling the interspaces of plates of biotite which surround *automorphic* crystals of augite or inclose them poikilitically." Of the most pyroxenic type, that of which an analysis has been cited, nothing is said as to the form of the augites; but their being spoken of as granular ("grenues") leads one to think that the augites are xenomorphic. We know many pyroxenites from elsewhere of this granitoid type of texture and, so far as my experience of them goes, they do not show evidence of being built around automorphic and euhedral crystal cores; though conceivably evidence of such an origin may well have been obliterated in the process of growth, if this were not zonal.

It will be evident that pyroxenites of the first type of Lacroix, with automorphic augites, would be quite in harmony with Bowen's theory of the settling of the heavy crystals in a magma (N. L Bowen, *Amer. Jour. of Sci.*, 1915, xxxix., 175). (The sinking of crystals of feldspar and their accumulation at the bottom of flows of obsidian were observed by Von Buch (Geogn. Beschr. Canar. Ins., 1825, 229), who mentions experiments made by a M de Drée, in which feldspar crystals settled to the bottom of a crucible. The matter is discussed by C. Darwin, about 1844 ("Geological Observations," 2nd. ed., 1891, 132-140), who attempts thus to account for the differentiation of trachyte and basalt) Bowen studied the sinking of olivine and pyroxene crystals, and the rising of those of tridymite, in artificial melts, and the striking way in which the first two sank and the third rose was sufficient proof of the actuality of the phenomenon and the relative densities of crystal and liquid. So far as I know, we have few data, at least exact data, on the densities of liquid lavas, but the point arises as to whether the augite crystals are really heavier than the liquid in which they occurred.

The density of the augite crystals was determined as 3·242 at 23°. The average density of the solid leucite tephrite of Vesuvius (cf. Roth, Abh. Berl. Akad. Wiss., 1877, 13; and Zirkel, Lehrb. Petrog., 1894, iii., 19. Roth gives the average as 2·77) may be taken as about 2·8, while vom Rath (vom Rath, *Z. deutsch geol. Ges.*, 1873, xxv., 240) gives the values 2·512 and 2·592 as the densities of the glassy crusts of Vesuvian bombs of 1872, and Lagorio (Lagorio, *Tscherm. Min petr Mitth.*, 1887, viii., 475) 2·319 as that of a Vesuvius obsidian. We may therefore provisionally accept a density of about 2 5 for the Vesuvius glass. As to the liquid lava, we have no data; but, assuming a density of 2·8 for the solid lava, we may conclude from the discussion of Daly (R. A. Daly, *Amer. Jour. Sci.*, 1903, xv., 277) based on Mellard Reade's and Barus' data as to expansion, that the molten lava would have a density of about 2·35. This does not take into account the presence of dissolved gases, which would unquestionably lower the density, and at the same time decrease the viscosity, very materially. It is clearly evident, therefore, that augite crystals, placed in such a leucite tephrite magma, would be much more dense than the magma, and would tend to sink, though the actual sinking of many of them would be more or less prevented by movements in the liquid, and by the possible presence of attached gas bubbles in the upper portions of the mass. Anyone who has made mineral separations with heavy liquids will appreciate the possibilities of disturbance of a "theoretically" perfect separation, adherent particles of the lighter minerals here replacing the gas bubbles of the magma.

But the occurrence of masses of rock of granitic texture, without euhedral crystals, or crystals formed freely in the body of the liquid, of the same composition as such crystals formed in what must have been a very similar magma and at the same volcano, seems to demand the recognition of some other factor than gravity, or at least one in addition to that of gravity.

This is not the place to enter into a discussion of the various kinds or causes of differentiation that have been suggested, but I must recall the case of Shonkin Sag and the explanation of its differentiation by fractional crystallisation advanced by the late Prof. Pirsson, which, it seems to me, Daly has not adequately met by an appeal to gravitative differentiation (L. V. Pirrson, *Amer. Jour. Sci.*, 1901, xi., 12; U.S Geol. Survey, *Bull.* 237, 1905, 188. Cf. Daly, "Igneous Rocks and their Origin," 1914, 223, 238). Pirrson and I held much the same views on these matters, and I feel inclined to revive a theory put forward many years ago (Washington, *Bull.* Geol. Soc. Amer., 1900, xi., 409, 414; *Jour. Geol.*, 1901, ix., 663), chiefly to account for the different types of laccolithic differentiation. This is based on fractional crystallisation, perhaps aided by convection currents, as Pirrson supposed, the crystallisation beginning at the rough walls, and the crystals of this portion (in the present case monomineralic) interfering with each other so as to produce a granitoid textured rock. Crystallisation of free floating crystals (therefore euhedral) in the magma could, and probably would, also go on simultaneously The process is analogous to the slow freezing of a bottle of salt solution, which begins at the walls, so that clear ice forms above, at the sides, and at the bottom, leaving finally a central core of highly concentrated solution. With the more complex rock magmas the process would be conceivably more complex than this, but the

same general principles would seem to apply. Unquestionably, the influence of gravity might or would be felt, especially on the loose floating crystals, but this would probably have less or no effect on the wall accumulations. The process is analogous to Daly's chilled border concept, but differs from this in that, according to Pirrson's and my hypothesis, the border crystallisation product does not represent the original magma, as conceived by Daly, but would be an "extreme pole of differentiation."

(To be continued.)

## BRITISH INDUSTRIES FAIR, 1921.

February 21—March 4.

In a few days' time the British Industries Fair, London, for 1921, will be opening its doors at the White City to the buyers of the world. This will be the seventh London Fair, and promises to surpass its predecessor even as that in its turn added to the roll of success. It is estimated that there will be some 3½ miles of stands displaying British goods at the White City. Since its inception in 1915, the record of the British Industries Fair has been one of continuous growth in scope, utility, and reputation. Started as a means of promoting the manufacture in the United Kingdom of articles previously made in enemy countries, the Fair made so instant an appeal and received such warm support from its exhibitors, that it has never looked back, and is now established in a predominant position among the great trade fairs of the world. The secret of this success is not far to seek; the British Industries Fair is a *business exhibition for business men.* Producing trades are carefully grouped for the convenience of the inspecting buyer, and these groups are again split up into sections and so housed and exhibited as to facilitate to the utmost a rapid and thorough survey of British production in any given line. The foreign buyer is invited by the Department of Overseas Trade, and invitations only extended to *bona fide* firms and representatives, thus enabling both buyer and seller to conduct their business unhampered by a crowd of sightseers. Participation in the Fair, limited to manufacturers in specified British trades, is both cheap and simple, offering equal opportunities to both large and small firms. This year's exhibitors cover both categories, and form the most representative body of British manufacturers ever assembled. Their names alone are a guarantee of the quality of the goods to be displayed and their keenness to exhibit is shown by the fact that the available space in every section of the Fair has been applied for several times over.

The goods to be displayed in the London Section include books, cutlery, silver and electroplate, jewellery, watches, and clocks, hard haberdashery, glassware of all descriptions, china, earthenware and stoneware, paper, stationery and stationer's sundries, printing, fancy goods, including travelling requisites and tobacconists' sundries, medical and surgical instruments and appliances, leather for the fancy goods, bookbinding, and upholstery trades, brushes and brooms, toys and games, sports' goods, scientific and optical instruments, spectacle ware and opticians' supplies, photographic and cinematograph apparatus and requisites, drugs and druggists' sundries, musical instruments, furniture other than metal, basketware.

The Birmingham Fair also opens on Feb. 21, at the Castle Bromwich Aerodrome. The oversea visitor will have the opportunity to inspect some 20 sections covering the trades for which that city is world-famous Every type of fitting for lighting and cooking, and a wide range of hardware, including household ironmongery will be on display, together with metal furniture and saddlery, indiarubber goods and motor accessories. In fact, almost every branch of the British metal industry will be represented.

The exhibits at the well-known Kelvin Hall, Glasgow, will include textiles of all sorts, ready-made clothing, hats, boots, carpets, foodstuffs, chemicals, and dyes. This Fair opens and closes a week later than the London and Birmingham Sections

So much for the home end of the Fair. A good show is guaranteed; what of the use to which it will be put? Never has the foreign buyer had a more favourable opportunity for purchasing in our markets. The tremendous demand prevailing in the home market early last year has fallen to below normal, contracts have had to be cancelled or curtailed, with the result that the British manufacturer has ample stock in hand to meet new orders. No opportunity has been missed by the Department of Overseas Trade and the organisers of the Birmingham and Glasgow Sections of bringing those favourable conditions to the notice of the foreign buyer.

With the financial support of the exhibitors, the Department of Overseas Trade has conducted a wide publicity campaign in the oversea press, in addition to the normal propaganda activities. Reports so far received promise excellent results. Invitations have been issued to some 60,000 overseas buyers of standing, and the same number of illustrated booklets, translated into eight languages, have been issued all over the world. Liberal use has also been made of showcards with the assistance of overseas banks, shipping companies and the Consular Diplomatic Officers of the Department in all parts of the world. Excellent reports as to the number of visiting buyers have been received from Scandinavia, where special conducted tours during the Fair are being arranged. From the United States, also, the prospects of a large number of visitors are favourable. Switzerland, Finland, Canada, and Italy are among countries where interest in the Fair is also reported as being considerable. Many committees, both official and unofficial, in this country are studying the question of the entertainment of the oversea visitor. During the period of the Fair, it is hoped that official foreign commercial missions will visit this country as guests of the British Government.

The White City not only provides the exceptional floor space necessary for the British Industries Fair (35,000,000 cubic feet are available), but has the merit of being easily accessible. The exhibition buildings are grouped between five railway stations, all giving direct access. Twenty minutes by taxi will cover the journey from all parts of the West End.

## THE THEORY OF RELATIVITY.

NO scientific subject has excited so much discussion in recent years as the Principle of Relativity developed by Lorentz, Einstein, and Minkowski. Since the work of Faraday and Clerk Maxwell, the existence of an all-pervading æther has been an accepted doctrine of physical science. The æther was conceived as stationary, yet all tests—like that of the classical experiment of Michelson and Morley—failed to detect the movement of the earth through it. FitzGerald suggested that the dimensions of the apparatus were affected by the movement. On the theory of the electromagnetic constitution of matter, Larmor and Lorentz worked out mathematically the consequences of this view. The conclusion was reached that no experiments could ever reveal absolute motion. Einstein showed that remarkable consequences as to the time and space followed from this proposition, necessitating a new mental picture of the physical universe. The details of this conception constitute his presentation of the Theory of Relativity.

Many physicists find it difficult to abandon the idea of the existence of the æther as they have come to think of it, and do not consider such a revolutionary change of thought is necessary as is involved in the complete acceptance of the principle. The different aspects of the theory are described in the important articles published in the special issue of *Nature* on February 17. The contributions constitute the most authoritative scientific statemen on relativity from different points of view yet published, and the number will be of permanent value.

The articles will include the following.—

"A Brief Outline of the Development of the Theory of Relativity" by Prof. A. Einstein.
"The Michelson-Morley Experiment and the Dimensions of Moving Bodies," by Prof. H. A. Lorentz, For.Mem.R.S
"Electricity and Gravitation," by Prof. H. Weyl.
"Theory and Experiment in Relativity," by Dr. Norman R. Campbell.
"The Metaphysical Aspects of Relativity," by Prof. H. Wildon Carr.
"Relativity and the Motion of Mercury's Perihelion," by Dr. A. C. D. Crommelin.
"Relativity: the Growth of an Idea," by E. Cunningham.
"Relativity and the Eclipse Observations of May, 1919," By Sir Frank Dyson, F.R.S.
"The Relativity of Time," by Prof. A. S. Eddington, F.R.S.
"The General Physical Theory of Relativity," by J. H. Jeans, Sec. R.S.
"The Geometrisation of Physics, and its Supposed Basis on the Michelson-Morley Experiment," by Sir Oliver Lodge, F.R.S.
"Non-Euclidean Geometries," by Prof. G. B. Matthews, F.R.S.
"On the Displacement of Solar Lines," By Dr. C. E. St. John.
"The Relation between Geometry and Einstein's Theory of Gravitation," by Dorothy Wrinch and Dr. Harold Jeffreys
Bibliography of Books and Pamphlets on Relativity.

## CORRESPONDENCE.

### DYESTUFFS (IMPORT REGULATION) ACT, 1920.

*To the Editor of the Chemical News.*

SIR,—The Council of the Institute of Chemistry have addressed a letter to the Board of Trade, enquiring whether licenses would be necessary under the Dyestuffs (Import Regulation) Act, 1920, for the import of small quantities of organic chemicals (including intermediate products used in the manufacture of dyestuffs, &c), required solely for research purposes. I enclose herewith a copy of the reply received.—I am, &c.,

RICHARD B. PILCHER
(Registrar and Secretary).

[Copy]

Board of Trade
(Industries and Manufactures Department
8th *February*, 1921.

SIR,—With further reference to your letter of the 28th January, regarding the Dyestuffs (Import Regulation) Act, 1920, I am directed by the Board of Trade to state that, whilst it is not possible to regard small quantities of organic intermediate products which may be required for research purposes as being outside the scope of the Act, the Board will be prepared to issue general licenses for the importation of such products to approved research institutions, covering periods of three months and limited only as to total quantities. This procedure will obviate the necessity for separate applications for a large number of small items, but it will be a condition of the issue of any general license that a detailed return shall be furnished at the end of the three months during which the license is in operation, of the quantities of each product actually imported under it.—I am, Sir, your obedient servant,

(Signed) PERCY ASHLEY

The Registrar & Secretary,
Institute of Chemistry of Great Britain & Ireland,
30, Russell Square, W.C.1.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. clxxi, No. 22, November 20, 1920.

CONSTITUTION OF THE PARAMOLYBDATES.—M. S. Posternak.—Delafontaine showed (*Arch Sc. phys. et natur.*, 1865, xxiii., 5) that the composition of ordinary ammonium molybdate and the corresponding salts of sodium and potassium could be expressed by the general formula

$$3R_2O.7MoO_3+NAg,$$

these salts being termed the paramolydates, in distinction to the ortho and metamolybdates. The latter are dibasic, whereas the paramolybdates are hexabasic. Blomstrand proposed $MO^{vi}(OMoO_2OR)_6$ as the formula for the paramolybdates. Copaux gave as the formula $R_6[MoO_2(Mo_2O_7)_3]$, both these expressions deriving the salts from a hexavalent molybdic acid

($Mo(OH)_6$), unknown by them. Rosenheim (*Zeit. f. anorg. Chemie*, 1916, xcvi, 139) brought forward a theory that for the most part the polymolybdates were derived from a hypothetic aqueous acid $H_{10}(H_2O_6)$, each oxygen atom being capable of replacement by a bivalent $MoO_4$ or $Mo_2O_7$ group, which gives two series of salts of more or less saturated acids $H_{10}[H_2(MoO_4)_6]$ and $H_{10}[H_2(Mo_2O_7)_6]$. Ordinary ammonium molybdate $3(NH_4)_2O.7MoO_3+4H_2O$, under this hypothesis becomes $(NH_4)_5H_5[H_2(MoO_4)_6]$, a pentabasic salt of aquahexamolybdic acid. This theory of Rosenheim's is subject to criticism, for the author has been able to prepare ammonium paramolybdate in the anhydrous state, showing that the $4H_2O$ given by Delafontaine's formula is water of crystallisation and not as in Rosenheim's formula part of the constitution. The author has also prepared two new ammonium salts intermediate between the para and metamolybdates; the mono and triammonium heptamolybdates $NH_4O(OH)_2MoO(O.MoO_2)_5.MoO_2(OH)+H_2O$ and $(NH_4O)_3MoO(O.MoO_2)_5O\ MoO_2(OH)$. The constitution of these salts show that ammonium paramolybdate should be written:—

$$(NH_4O)_3MoO(O.MoO_2)_5O.MoO(ONH_4)_3+4H_2O.$$

The author then gives a short account of the method of preparation of anhydrous hexaammonium heptamolybdate, mono and triammonium heptamolybdates.

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Vol. clxxii., No. 2. January 10, 1921.

TETRABASIC POLYMOLYBDATES.—M. S. Posternak.—The author in examinng the changes of composition brought about by ammonium phosphomolybdate, arrived at the conclusion that molybdic acid, in a strong acid solution, contained tetravalent molybdenum, in fact, he prepared trihydroxyammonium tetramolybdate.

$$NH_4O(OH)_2MoO(O.MoO_2)_3OH+5H_2O,$$

by mixing 100 cc. of 10 per cent solution of ordinary ammonium molybdate with 25 cc. of 2 normal $H_2SO_4$ and 10 grms. of ammonium sulphate. This salt loses $5H_2O$ in a sulphuric atmosphere, and still a further $H_2O$ when heated in an oven to 130°-160°. Rosenheim (*Zeitsch. f. anorg. Chemie.*, 1897, xv., 180) who has prepared the same compound, and estimated the water by difference, called the salt an octomolybdate $(NH_4)_2O.8MoO_3+13H_2O$, in accordance with the old classification of Ullik (*Ann. der Ch. und Pharm.*, 1867, cxliv., 204, 320). The properties of this salt are important for the polymolybdate theory. Dissolved in water, it becomes unstable; these aqueous solutions warmed on a water-bath or maintained at 40° in an oven, deposit short needles having the composition of a trihydroxyammonium pentamolybdate.

$$NH_4O(OH)_2.MoO(O.MoO_2)_4OH,$$

an anhydrous salt losing an $H_2O$ molecule from its constitution on being heated to 130°-160°, acting similarly to all the series of salts having two neighbouring hydroxyl groups. Rosenheim and Felix (*Zeitsch. f. anorg. Chemie.*, 1913, lxxix., 292) considered it to be a decamolybdate

$$(NH_4)_2O.10MoO_3+3H_2O.$$

The mother-liquors on being allowed to crystallise give a hexammonium dodecamolybdate If the tetramolybdate is allowed to recrystallise twice in four parts of water at 75°, taking care to filter off the insoluble, it is transformed into trihydroxyammonium tridecamolybdate

$$(NH_4O)_3MoO(O.MoO_2)_{11}O.MoO(OH)_3+19H_2O.$$

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## NOTES.

INSTITUTE OF METALS.—At the Annual General Meeting, March 9 and 10, 1921, the following papers are expected to be submitted in the order given:—

Wednesday, March 9 (Morning Session, 10.30 a.m. to 1 p.m.)—(1) "Stages in the Re-Crystallisation of Aluminium Sheet on Heating, with a Note on the Birth of Crystals in Strained Metals and Alloys," by Prof. H. C. H. Carpenter, M.A., Ph.D., A.R.S.M., F.R.S., Past-President, and Constance F. Elam, Member (London). (2) "Some Notes on Calcium," by P. H. Brace (East Pittsburgh, Pa., U.S.A.), (presented by Dr. J. L. Haughton)

Wednesday, March 9 (Afternoon Session, 2.30 p.m. to 4.30 p.m.). (3) "Plastic Deformation of some Copper Alloys at Elevated Temperatures," by Prof. C. A. Edwards, D.Sc., Member, and A. M. Herbert (Swansea). (4) "The Action of Reducing Gases on Heated Copper," by H. Moore, O.B.E., B.Sc., Member, and S. Beckinsale, B.Sc. (Woolwich).

Thursday, March 10 (Morning Session, 10.30 a.m. to 12.30 p.m.). (5) "The Season ~~Cracking of~~ Brass and other Copper Alloys," by H. Moore, O.B.E., B.Sc., Member, S. Beckinsale, B.Sc., and Clarice E. Mallinson, M.B.E., B.Sc. (Woolwich). (6) "Constitution of the Alloys of Copper with Tin, Parts III and IV.," by J. L. Haughton, D.Sc., F.Inst.P., Member (Teddington)

VEGETABLE ALKALOIDS.—Very often, as is known, the hydrogen of the hydroxylic aminic and iminic groups is replaced by alcohol or alcoholic radicals. Messrs. Ciamician and Ravenna demonstrate that the latter augment the noxious action of the fundamental substances which contain them, but when the fundamental compound, non-toxic, is normally present in the plant, its derivatives are not so. In any case, the most poisonous substances are those which best resist the action of oxidising ferments and the effect of the organic substances on plants should be in relation to the resistance they offer to their elimination.—*Comptes Rendus*, November 2, 1920.

THE COUNCIL of the University of Birmingham, in their Annual Report, state that Sir John Cadman felt compelled to resign his professorship of mining engineering on his appointment as adviser to the Cabinet on questions affecting coal and petroleum. As it was not found possible to secure a suitable occupant for the Chair, Sir John had accepted an invitation from the Council still to act as professor in this department and adviser in the department of petroleum technology, giving such time to the office as his other duties permitted, with an honorarium of £500 a year.

ROYAL INSTITUTION.—The Managers of the Royal Institution, in accordance with the Actonian Trust Deed, have awarded the Actonian Prize to Prof.

G. E. Hale, D.Sc., LL.D., F.R.S , Director of the Mount Wilson Solar Observatory, for his contributions to solar physics

Problems of Modern Science.—The principal subject chosen for the lecture on "Modern Problems in Chemistry" at King's College (University of London), was the development of the chemistry of natural products. The lecturer introduced the subject by giving an outline of the history of organic chemistry from this standpoint, and showed how the ideas of the structure of carbon compounds had grown, and how these had been applied to the artificial production of many substances obtained originally from natural sources. After a description of the achievements of synthetical organic chemistry in this field the lecturer explained how recent efforts of chemists had been directed to the study of the processes actually employed by the plant. The occurrence of formaldehyde in the leaves of plants had been demonstrated and this substance had been artificially produced from carbonic acid and water under the influence of light and from carbonic acid by the action of magnesium. In this way a probable explanation was obtained of the initial stages in assimilation of carbon by the living plant. Moreover, it had been further shown that formaldehyde may be converted into sugars and thus an indication given of how the more complex substances of this kind may be produced in plant life. The nature of enzymes was also described, and their probable function in the chemical changes taking place in plants was pointed out. Finally, the lecturer described the chief problems which await immediate solution in this field of research.

Properties and Constitution of the Group $OCCl_3$.—Messrs. Kling and Florentin specify in this note the properties of the group $OCCl_3$ which they studied subsequently to their researches on the products of chlorinated substitution of chloroformates.—*Comptes Rendus*, January 3, 1921.

Mineral Resources of Great Britain.—The Ministry of Agriculture and Fisheries desire to give notice of the publication of Volume No. XIV. of the Special Reports on the Mineral Resources of Great Britain which have been prepared by the Director of the Geological Survey in response to numerous enquiries that arose through conditions brought about by the late war. Price 8s. net. This volume contains a brief but comprehensive account of the geology of the fire-clay deposits of great Britain, with especial reference to those beds which are at present employed for the manufacture of fire-bricks, furnace-linings, and other refractory materials. The industry is an old-established one, and, especially during the war, was of great national importance. The British fire-clays are described according to the counties in which they occur, and particulars are given of every deposit that is known to be of economic value. Fortunately for the country there is an abundant supply of fire-clay, and the reserves are large, while the variety of clays is such that almost every use to which the mineral is put can be adequately provided for from home sources. This volume is a sequel to the Memoir on Siliceous Refractories previously published, and it is intended to issue another part containing chemical analyses and furnace-tests of many of the best-known fire-clays. Copies can be obtained from any Agent for the sale of Ordnance Survey and Geological Survey Maps, or through any Bookseller, or from the Director-General, Ordnance Survey Office, Southampton.

New Method for Colorimetric Analysis of Small Quantities of Uranium.—This method by Muller is based upon the formation of a red compound with salicylic acid (5 cubic metres of the salt of uranyl and 5 of a 2 per cent soda solution of salicyclic acid. A uranyl nitrate solution is treated in the same manner, and comparison made with the Dubose colorimeter. Thus the percentage of uranium can be estimated to about 0·02 per cent. The solution must not contain free mineral acids, and even a large proportion of acetic acid is inconvenient. Thus acid solutions should be treated with excess of sodium acetate, the acid being then eliminated by ebullition. There must be no iron. Alcohol and acetone are obstacles.—*Chimie et Industrie*, November, 1920.

## New Patents.

This List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W C.2, from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously

*Latest Patent Applications.*

3377—Akt-Ges fur Anilin-Fabrikation—Process for protecting animal fibres in treating them with alkaline liquids. Jan. 27th.

3369—Bawden, C.—Manufacture of ortho-nitro phenol and para-nitro phenol. Jan. 27th.

3370—Bawden, C.—Separation of ortho.- and para-nitro chlor benzines from mixtures thereof. Jan. 27th.

3371—Douse, D. F.—Manufacture of ethyl-chloroformic ester. Jan. 27th.

2921—Freeth, F. A.—Production of ammonium chloride and sodium carbonate. Jan. 24th.

3032—Prager, H. A.—Manufacture of naphthalene compounds. Jan. 24th.

3033—South Metropolitan Gas Co.—Manufacture of ammonium sulphate. Jan. 24th.

*Specification published this Week.*

157578—Sidgwick, N. V, Plant, S. G. P. and Boake Roberts & Co. Ltd.—Preparation and manufacture of di-ethyl sulphute.

*Abstract Published this Week.*

*Acetic Acid.*—Mr. H. Dreyfus of Waterloo Place, London has recently been granted a Patent No. 154680 for improvements in the manufacture of acetic acid by oxidation of aetaldehyde at 10-20° C., the catalyst employed is the residue which remains after igniting the carbon from animal charcoal, with or without the addition of sodium acetate. As the residue mainly consists of calcium and magnesium phosphates, it may be replaced by a mixture of these compounds with or without small quantities of lime, silican dioxide, and fluorides.

Messrs. Rayner & Co, will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

## MEETINGS FOR THE WEEK.

*Monday, February* 21.

Royal Society of Arts, 8. "Applications of Catalysis to Industrial Chemistry," by Dr. Eric K. Rideal.

*Tuesday, February* 22

Royal Institution, 3. "Darwin's Theory of Man's Origin (in the Light of Present Day Evidence) by Arthur Keith.
Society of Chemical Industry, (At Glasgow).
Institution of Petroleum Technologists, 5.30.
Institution of Electrical Engineers, 7. (At Leeds and Manchester).

*Wednesday, February 23.*

Royal Society of Arts, 8. "Premature Elevators in Theory and Practice" by Dr. William Cramp.
Society of Chemical Industry, 7. (At Nottingham).
Institution of Electrical Engineers, 7. (At Birmingham).

*Thursday, February 24.*

Royal Institution, 3. "Mason Bees" by Frank Balfour Browne
Institution of Electrical Engineers 6.

*Friday, February 25.*

Royal Institution, 9. "The American Civil War," by John Buchan.
Physical Society, 5

*Saturday, February 26.*

Royal Institution, 3. "Spectroscopy—Celestial Spectroscopy," by A. Fowler

## NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemical Apparatus, &c., for review or notice to be addressed to the EDITOR.

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THE CHEMICAL NEWS.

VOL. CXXII., No. 3176.

# THE THEORY OF AUXILIARY VALENCIES AND "WATER OF CRYSTALLISATION."

By H. T. F. RHODES.

THE theory of auxiliary valencies, first enunciated by Werner, was designed to account for the existence of some compounds that have been variously termed "molecular complexes" and "compounds of higher orders," &c.

Apparent abnormalities in valency undoubtedly exist, and strictly speaking, it is very doubtful if, in the present state of our knowledge any definite statement about valency can be made, since, particularly with regard to "water of crystallisation," we are faced with a large and increasing number of compounds that seem to suggest that their capacity for affinity is much greater than the ordinary facts concerning their valency would lead us to suppose. For example, it is only necessary to mention the "alums" that crystallise with twelve molecules of water; and although it may be argued that this water is not in chemical combination with the salt, it can only be answered that—save perhaps in some cases which will be considered under "Conclusions"—we have no evidence that it is not; and on the other hand we are faced with the fact that these salts combine with a definite quantity of water. Indeed, all the evidence goes to show that these are, in some sense, chemical compounds. For example, great heat is generated when water comes into contact with dehydrated salts—copper sulphate is a notable example; and also in connection with this same salt there is the question of its sharp changes in vapour pressure, corresponding to well-defined hydrates when the anhydrous salt is treated with a water vapour in a closed vessel; indirect evidence that favours this view.

A short discussion of Werner's theory will not be out of place, and is, indeed, necessary to the subject before us.

The theory has given rise to some criticism, and the author himself—whose untimely death we have reason most deeply to regret—was among those who admitted the difficulties it involved. The theory is concerned with the idea that simple molecules possess an residual affinity in virtue of which more complex molecules can be constructed. This property belongs to the nucleus atom; for example, the oxygen atom of water, the sulphur in sulphur trioxide. It is postulated, however, that this residual affinity cannot effect a combination which falls within the definition of normal valency, although it is not supposed that the mode of action is different. Werner's co-ordination number is defined as the binding power that the primary and secondary valencies can together effect.

This would seem to be a fair definition, and even before discussing the question of the constitution of compounds, a formidable difficulty presents itself in the manner that save for the fact that secondary valencies seem to be in some sense a molecular phenomenon, it is difficult to draw a distinction between the two kinds of valency; and very properly, even this molecular question is tolerant of no loose interpretation, since Werner's definition of the co-ordination number insists upon this central atom as indeed it must, in order to save the existing definition of valency from grievous violence. This in itself tends to support the idea that there is no difference between the two kinds of valency, and as a corollary it seems difficult to escape the conclusion that auxiliary valencies have no real existence.

On the other hand, it is possible to assume that the auxiliary valencies do not differ in nature but in degree; and it is this aspect of the case that will be considered in the light of some of Werner's structural formulæ.

Werner assigns to ammonium chloride the structural formula:—

$$\left[\begin{array}{ccc} H. & & .H \\ & N & \\ H\cdot & & \cdot H \end{array}\right] Cl$$

that is to say that nitrogen is normally tervalent in ammonia and that it possesses one secondary valency making its co-ordination number four. Now if a difference in degree between primary and secondary valencies be admitted, then the four that include one that is weaker than the others operate with the four hydrogen valencies that are (because of heir normality) equal. It is impossible to discuss here the difficulties that this involves, but *prima facie* the conclusion is unsatisfactory. It is answered by the fact that a state of equilibrium may be supposed to exist, and undoubtedly under such circumstances some state of equilibrium must prevail if we are not to assume a kind of hysterisis, but it does not destroy the uncomfortable conclusion that the nucleus is fundamentally weak. But the position assigned to chlorine atom makes the difficulty the greater. It is amenable to the same objection (although not for the same reasons, in particular) that Friend (Friend, *Trans. Chem. Soc.*, 1916, p. 715) has alleged against the position of the chlorine atoms in hexamine cobaltic chloride and monochlorpentamine cobaltic chloride "since it hovers in an indefinite manner around the nucleus as a whole." In fine, such a formula suggests instability, an instability that experiment does not confirm. The comparative ease with which ammonium chloride dissociates is not evidence of instability, since it is impossible to judge the ammonium salts by a standard to which they are unqualified to conform. Taking into consideration the complex nature of the basic radicle, the ammonium salts are very stable.

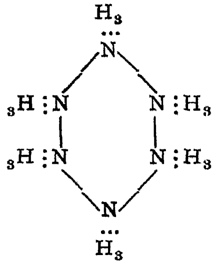
The difficulty is at least as great in the case of those salts that contain "water of crystallisation." Werner has assumed that the same principle is applicable, and he has accordingly written the formula of hydrated magnesium chloride, $Mg.Cl_2.6H_2O$.

$$Cl\left[\begin{array}{c} OH_2 \\ {}_2HO\cdot\;\vdots\;\cdot OH_2 \\ \quad Mg \\ {}_2HO\cdot\;\dot{}\;\cdot OH_2 \\ OH_2 \end{array}\right]Cl$$

which gives to magnesium a co-ordination number of six. It is true that magnesium chloride is unstable and that water cannot be removed from it without decomposition, but in order to establish the validity of the hypothesis it should be true of all

such salts, or of nearly all, and it is not; since, in general, those salts that contain six or more molecules of water are not on that account the less stable. The foregoing all tends to show that the case for the co-ordination number is very weak, and we are driven to the conclusion, therefore, that some modification is necessary.

Friend's heterocyclic theory of valency (Friend, *Trans. Chem. Soc.,* 1909, xciii., 1006; and 1908, 260, xciii., 11, 166, 441, 454) has been advanced to overcome these difficulties. The ammines are discussed and the structure



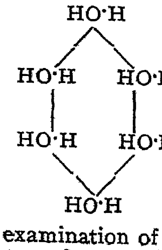
suggested for the ammine group.

This overcomes the difficulty with regard to these compounds, and is certainly the most satisfactory theory yet advanced.

In dealing with the question of water of crystallisation, a like assumption has been made by the present author, but it seems not improbable that the exercisation of some force (hereafter called molecular affinity) may hold the hydroxyl ring. Werner has credited, for example, the chlorine atoms in $MgCl_2.6H_2O$ with this property, but to say the least, this is most undesirable, since it is necessary under these circumstances to suppress the valency of chlorine. On the other hand, no such objection can be alleged in the case of the ring, since it possesses no free valency. It is doubtful, nevertheless, if such a conclusion is sound, but it has been included as a possible alternative.

Armstrong suggested that modifications of water existed on the assumption that oxygen may be quadrivalent, thus :—

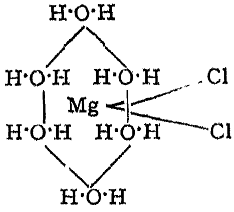
The evidence he adduces is certainly worthy of consideration, and it intimately concerns the question before us. A ring structure has also been assigned to water (see Kohlrauch, *Proc. Roy. Soc.,* 1903, lxxi., 338) :—



Now from an examination of a list of those salts that contain water of crystallisation reveals the interesting and significant fact that the most numerous class is that which contains salts with six, seven, or twelve molecules of water.

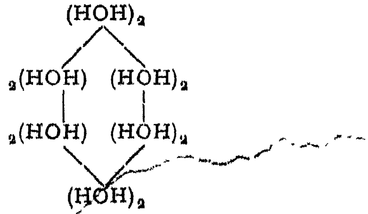
| $H_2O$ | Per cent. | $H_2O$ | Per cent |
|---|---|---|---|
| 1 ... ... ... ... | 4 | 10 ... ... ... | — |
| 2 ... ... ... ... | 6 | 11 ... ... ... | — |
| 3 ... ... ... ... | 8 | 12 ... ... ... | — |
| 4 and 8 ... ... | 16 | 13 ... ... ... | — |
| 5 and 10 ... .. | 19 | 14 ... ... ... | — |
| 6, 12, 7 ... ... | 38 | 15 ... ... ... | 2 |
| 7 ... ... ... ... | — | 16 ... ... ... | — |
| 8 ... ... ... ... | — | 17 ... ... ... | — |
| 9 ... ... ... ... | 4 | 18 ... ... ... | 3 |

$X.6H_2O$.—If the ring structure be allowed, this at once disposes of salts that contain six molecules of water. For example, the hydrate of magnesium chloride becomes :—

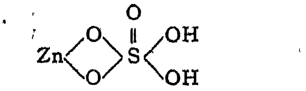


The considerations for and against this and the succeeding structural formulæ will appear under "Conclusions."

$X12H_2O$.—In this case the molecules may be regarded as polmerised thus :—



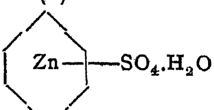
* * The little evidence that we possess is in favour of the idea that those salts containing seven molecules of water, which are principally sulphates, have one molecule in normal combination :—



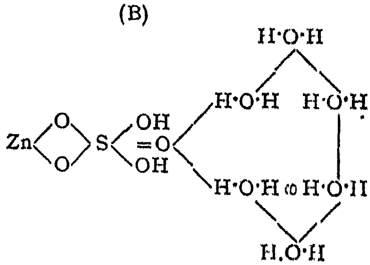
* * Zinc sulphate loses six waters at 100° C. and the seventh at red heat.

$X.7H_2O$.—Two possible formulæ would seem to suggest themselves therefore :—

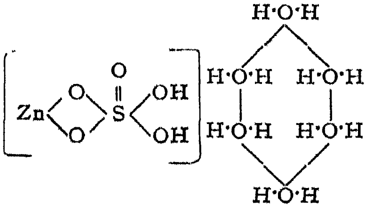
(A)



(B)



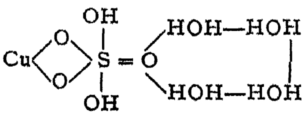
"A" appears to be the sounder of the two formulae as the second may seem to be unduly speculative; but it is included as an alternative the better to illustrate and to compare with one of the formulæ it is proposed to assign to copper sulphate—for sufficient reason, as will be seen when salts containing three molecules of water are discussed. In the second place the structure below is illustrative of this theory of molecular affinity. It is unnecessary and it may even be undesirable to suppose that the affinity is manifested about the hydroxyl, since it has been assumed that affinity is the product of the molecule as a whole, and the position of the hydroxyl ring may therefore be indefinite. But at the same time, if combination with itself be a property of water under certain conditions, there is something to be said for the attachment of the ring at that part of he molecule where the elements of water already exist.



X.$5H_2O$.—Some sulphates are associated with five molecules of water, and of these copper sulphate is a convenient example. As with zinc sulphate, one molecule of water is regarded as being in normal combination, and for the same reason. Formula A is probably more sound, but formula B is illustrative of the principal that it may be justifiable to include in the aqueous ring groups other than HOH groups

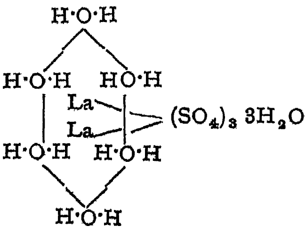
(A)

(B)

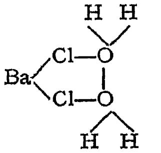


X.4HO and X.8HO.—These hydrates seem to call for no particular comment since they may be regarded as analogous to formula A above, less the molecule of combined water.

X.9HO.—It is interesting to observe that nine waters of crystallisation are associated with the "ic" sulphates, notably those of lanthanum and iron. And since they might be assumed to hold in combination three molecules of water, normally, the hydroxyl ring may in this case be applicable .

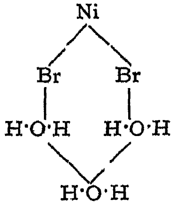


X.2HO.—This modification need not detain us long, since most of the salts are halides to which the formula below—quoted in most modern text-books— may be assigned.



This formula assumes, of course, the tervalency of chlorine, and quadrivalency of oxygen.

X.$3H_2O$.—In connection with those salts that contain three molecules of water, an interesting question presents itself. Their number is small, and for the most part they can be explained by the assumption that the water is in true hydroxyl combination; but among their number is a halide of nickel. This might be represented by the formula :—



This introduces the point as to whether it is justifiable to allow substitutions in the hydroxyl ring, for, granting this, formula B for copper sulphate may also be accepted as an alternative.

It only remains to allude to those salts that possess fifteen or eighteen molecules of water. Aluminium nitrate and aluminium and chromium sulphates correspond respectively, and are, it would seem, the only examples. Aluminium sulphate may be assumed to hold in true combination six molecules of water, and the remaining twelve molecules may form a polymerised hydroxyl ring, but it is extremely doubtful if there be any grounds for supposing that the nitrate can combine with water in any proportions, nor, if it be possible, does any ring formula prove itself *ad rem.* These salts of aluminium are, however, isolated exceptions.

(To be continued)

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ROYAL SOCIETY.—At the meeting of May 12, a Discussion on "The Quantum Theory of Line-Spectra" will be opened by Sir Ernest Rutherford, followed by Dr. N. Bohr.

ROYAL INSTITUTION.—On Saturday, March 5, at 3 o'clock, Sir Ernest Rutherford will deliver the first of a course of three lectures at the Royal Institution on "Electricity and Matter," and on Tuesday, March 8, Dr. G. C. Simpson, Director of the Meteorological Office, commences a course of two lectures on the "Meteorology of the Antarctic." The Friday evening discourse on March 4 will be delivered by Mr. W. A. Tait on "Severn Crossings and Tidal Power"; on March 11 by Dr. J. Freeman on "Medical Idiosyncrasies"; and on March 18 by Sir Frederick Bridge on the "Researches of a Musical Antiquarian."

## THE ALLUVIAL DIAMONDIFEROUS DEPOSITS OF SOUTH AND SOUTH-WEST AFRICA.*

By FRED. C. CORNELL, O.B.E.

In 1867, during a period of the greatest depression, in South Africa, when droughts of exceptional severity had killed off a large proportion of the flocks and herds, when a new and greatly resented duty upon Colonial wines had practically resulted in the loss of the Home market, and when, in short, prospects appeared most gloomy, a new lease of life was given to the country by the discovery of diamonds; a discovery which, pooh-poohed at first, was soon amply confirmed, and which was to bring about an industry of tremendous wealth, and of world-wide importance.

The first diamonds were discovered in the district of Hope Town, near the Orange River, but the bands of adventurous spirits which the discovery attracted to the spot, soon wandered to the banks of the Vaal River, where finds were much more plentiful; and it is along the latter river and not the Orange, that the principal "River Diggings" are to be found.

At first attention was only paid to the gravel adjoining the actual banks of the river, where, by laborious hand-washing, and the primitive methods of the gold fossicker, a modicum of good stones were found, and when, in 1870, the precious stones were found in greater abundance on the farms, Du Toits Pan and Bultfontein, at a considerable distance from them, the deposit was still thought to be a nalluvial one; for I need hardly mention that up to that time diamond-bearing pipes were unknown, and the world's supply of the precious stones, either from the East or from Brazil, had always been obtained from gem-bearing gravel.

And for a time these new deposits were known as the "Dry Diggings" in contra-distinction to those near the actual river, and they were worked by individual diggers, but it was soon found, not only that they were much richer in diamonds than the river gravel, but that their matrix was neither a gravel nor an alluvial deposit at all. These spots, in short, were the rich mines of the Kimberley of to-day, well-defined volcanic pipes, which have since proved of great depth and importance, and to-day provide the vast bulk of the world's output of diamonds.

Their history does not belong to a paper such as this, and I can only touch upon them. For a time the individual diggers flocked to them, and the River Diggings were almost abandoned, but with the recognition of their enormous value came the gradual elimination of the digger, whose place was taken by syndicates and companies, culminating in the huge combine of to-day.

Meanwhile the squeezed-out digger had drifted back to the banks of the Vaal, and for many years the district in the vicinity of Barkly West was their headquarters. Other small townships sprang into being as the result of "ruches" following the finding of good stones, notably at Windsorton, Hebron, Klipdam, Pniel, Gong-Gong, and dozens of smaller mining camps, but up to 1907 the diggings had practically been confined to Griqualand West. In that year, however, finds in the vicinity of Bloemhof, a considerable distance upstream, and in the S.W. Transvaal, led to a spread of the diggers in that direction, and in 1910, an extraordinary rush took place to that township, the population of which increased within a few weeks from some 4,000 whites, to nearly 16,000—principally diggers. Finds continued to be made even farther north, and it has been estimated that this diamondiferous area, which extends to Schweizer Rencke, some 35 miles farther north, and to nearly as far east as Klerksdorp, covers an area of some 2,000 square miles.

The principal diggings along the Vaal River, therefore, may be roughly divided into the "Higher" and "Lower" diggings, and may be said to extend from near Klerksdorp in the north, to the Junction of the Vaal and the Orange near Douglas, in the south and for varying distances inland from the banks.

Along this 200 mile stretch of river the gravel, often for miles away from the actual stream of to-day, has been burrowed into as though by an army of gigantic moles; heaps of debris, tailings, and the scrupulously cleaned and graded little pebbles that have been sorted over and over again as "wash," covering the whole of the country, especially in the vicinity of the better-known diggings.

Whilst the permanent river townships, such as Barkly West and others I have enumerated, are the centre of the industry (if it can be called one), it is no uncommon thing for the news of a big find some miles away to cause a rush to that locality to the depletion of the permanent settlements; and these rushes, spasmodic, and seldom resulting in many good finds except those that called them into being, are the scene of the most fevered activity. Tents appear as by magic, wagons, Cape-carts, and all sorts of other vehicles arrive and are used as a living place by their digger owners; stores and "hotels" of the flimsiest description are run up, and these at any rate usually thrive.

In short, a new digging, or a rush back to an old spot long since abandoned (as often happens), is the mining camp of the old days of California, or of Australia, over again. There is, however, but little of the rowdiness that belonged to those days, for the diamond digger is as a rule a most law-abiding person, and the six-shooter is conspicuous by its absence.

The diamonds are sparsely and unevenly distributed in the gravel, and their source remains undiscovered and still somewhat of a mystery. For a time the generally accepted theory was that they had been washed from the Kimberley pipes by the Vaal having at some period flowed through or over, the latter, and then been spread over the country with the gravel by subsequent floods or the changing of the river's course. But this theory has long since proved untenable. There is no evidence that the Vaal ever actually ran through the pipes; and again, not only have the diamond gravels been found far to the north—and upstream—of any of the Kimberley pipes, but the diamonds found in the gravel are very dissimilar from those of the mines, and easily distinguishable by an experienced eye.

*Journal of the Royal Society o Arts*, January 21, 1921.

Another theory, and one which appears highly probable, is that at a very remote period, glacial action denuded certain still undiscovered pipes of hundreds of feet of diamond-bearing magma, which, in its slow journey across the country, has been deposited where geological conditions or formation have been favourable, and that subsequent fluvial action has effected still wider distribution, which has culminated near the present river.

Of glacial action there is abundant evidence in the vicinity of the river itself, notably near Windsorton, Hebron, and Pniel. Another theory which has been advanced by certain geologists is that the diamonds were not formed in Kimberlite, but that they have weathered out from a peculiar amygdaloidal diabase, which outcrops in many places on the river bank, and which shows steam vesicles filled with agate, chalcedony, and other forms of silica in nodules—many of which in a loose state are found in the gravel in conjunction with the diamonds. The gravel, whatever its source may have been, presents many features in common; even in spots so widely separated as those of the Higher and Lower Diggings, the deposits near the Harts River in the vicinity of Taungs, those but recently discovered at Rouxville on the Orange River, the huge terraces near the mouth of the Orange (many hundreds of miles from the last-named deposit) and the deposits, so rich in tiny gems, of the sandy coast of what was recently German South-West Africa.

In the vicinity of the Vaal River diggings, the gravel varies in depth from a few inches to as many feet, and this "top" or superficial "wash," which is usually a loose, easily-worked gravel, held together with reddish loamy soil, often covers a distinct stratum of a different gravel; generally consisting of much larger stones, or boulders, often ten or twelve feet in depth, very much more compactly bound together, and usually of a greyish colour. In places this lower deposit becomes practically a conglomerate; the cementing matter being so hardened as to make it extremely difficult to break up. But whether "surface" gravel or "deep" gravel, the smaller water-worn pebbles that go to make up the diamond-bearing portion of it, are always, and everywhere, practically the same.

They are of agate, jasper, nodules of chalcedony, and other forms of silica, fragments of granite, and shale, and above all of banded ironstone, the latter providing the "bandtom" of the digger, an "indication" sought by him everywhere.

The method of searching for the diamonds is, with certain local and unimportant modifications, practically the same on all the diggings. Discarding the primitive and laborious process of hand-sieving and washing, which is rarely used now, except by the very poorest diggers, and which has very little chance of success, the usual procedure is as follows.

The would-be digger, having proved to the satisfaction of the Mining Commissioner and Diggers' Union, that he is a fit and proper person to hold a license, and having obtained both that and a claims licence, pegs out a claim on the chosen spot, which must be part of a "proclaimed" area open to digging. The size of the claims varies somewhat, but they are usually 30ft. square, and the digger is by no means restricted to one; indeed, granted space be available, he can peg out as many as he cares to pay for, provided he works them within a specified time. He usually employs a gang of some six to a dozen natives; these "boys," as they are called, are usually Kaffirs, Xosas, or Basutos, who are to be obtained easily in the neighbourhood of the better-known diggings, especially in the summer season. They are paid a wage which is periodically fixed by the "Diggers' Union," and is usually in the vicinity of £1 per week, in some cases being supplemented by a ration of "mealie-meal."

These men are, many of them, expert diggers, keen-eyed and not always honest, and usually require watching very closely. With picks and shovels the gang, under the supervision of the digger, excavate the gravel down to "bedrock," which may be an actual bottom of shale, or a sandy stratum overlying another layer of gravel. The loosened gravel is "roughed" through screens of large mesh, which reject the larger stones. The boulders are thrown aside, and the resultant finer gravel is then sieved through a rocking machine called a "*bébé*," not as most people believe on account of its fancied resemblance to a cradle, but from the name of the Frenchman Bébé, whose invention it was.

This machine is a long, fine-meshed sieve, some 6ft. or so in length, by about 2ft. in width, slung by chains from a supporting framework, at a slant; the higher end being near the operator. At this upper part provision is made for a jumper sieve to rest, and the mesh of this sieve varies from half-an-inch to perhaps three-quarters. Into this sieve the previously "roughed" gravel is thrown, usually from a bucket, and the operator holding the upper sieve firmly on the *bébé*, rocks the whole backwards and forwards. The finer gravel and sand fall through on to the inclined sieve of the *bébé*, and travel slowly down it, the sand falling through on its way, and only the fine gravel being shot from the lower end on to an evergrowing heap, which forms the "wash" for the next process, while the coarser particles remaining in the jumper, are, after a glance for a possible Cullinan, thrown aside to make place for the next bucketful. The next process, and one which only takes place periodically, and when a large amount of "wash" has been accumulated, is the actual washing by means of a rotary machine.

These machines consist of an iron pan, some 4ft. to 6ft. in diameter, and about 1ft. in depth, fixed in an extremely stout wooden framework, in which a series of spokes or arms, set with knives, are rotated by a crank. An inclined trough or "feed box" leads to the pan, and into this box the wash is fed, but not in a clean state. Instead, it is mixed with the necessary quantity of sand, or loam, and water, into a mud, the consistency of which is a very vital factor in the ultimate recovery of any diamonds. Once the "wash" is in progress, the mixture is being constantly worked up in the upper end of the feed-box, and this work, which is an extremely dirty and unpleasant task, is usually carried on by one or two of the more experienced natives, who convert sand, water, and gravel, into a glorified mud-pie, as they feed it into the maw of the constantly rotating knives.

The result of keeping this mixture at a proper consistency is that once the machine is full, the

lighter stones, kept in suspense by the constant rotary movement, run over the edge of the inner portion of the pan, and flow away in a sluggish stream of tailings, only the heavier stones falling to the bottom. A little trap in the lower rim of the pan allows of the residue being occasionally tapped, and it is in this that the diamonds should be found. The final washing and sorting of this residue is an extremely important and delicate task, and is usually carried out by the digger himself. For this process a specially constructed sieve, known as a gravitating sieve, is used, it has an extremely rigid steel mesh, and the proper handling of it is the culminating test of the experienced digger.

Half filling it with the wash from the tap, he holds it quite level and firmly with both hands and rotates it just beneath the surface of the tubs of water, which form an essential part of his equipment, washing away the mud, until in the final water, when the gravel is perfectly clean, he finishes with a peculiar movement, only to be acquired by constant practice, and which has the effect of concentrating the heavier particles into the exact centre of the bottom of the sieve.

Then with an adroit movement he turns the sieve upside down, brings it down with a bang upon the sack-covered sorting table and lifts it, leaving the clean gravel exposed. If the sieve has been properly "thrown," as it is termed, the centre will show a well-defined circle of concentrates much darker in colour than the bulk of the mass, and if the whole series of operations has been properly performed throughout, the diamond should be found amongst these comparatively few little stones.

These dark stones are principally composed of water-worn pebbles, of banded ironstone, already alluded to as "bandtoms," and of approximately the same specific gravity as the diamond, namely, 3·5.

It will thus be seen that the whole system is based upon gravitation, and the gradual elimination of the lighter stones; and although in addition to the rotary washing machines which I have described, there are other mechanical contrivances for washing and treating the gravel (notably the so-called "gravitator"), the principle is practically the same.

The sorting is usually carried out by the digger himself, who after a glance at the little circle of dark bandtoms, carefully scrapes and turns over the stones with a knife or other implement, and this process continues until the whole of the "wash" has passed through the machines and over the sorting table.

But the digger must not be disheartened if days and days of this laborious work ends in the "wash" proving a blank; he may find not only a heavy deposit of the accompanying bandtom, but may be cheered by the presence of garnet, olivine, and ilmenite (called "carbon" by the digger) in his concentrates, but the diamond itself may be absent. Indeed, not only his first "wash" may prove a blank, but the whole of his claim or claims; and yet within a few yards his neighbour may have struck a rich patch and be turning out a small fortune.

For nothing is so uncertain as diamond digging. The distribution of the stones in the gravel is so irregular that the finding of several near together affords no criterion as to the adjoining gravel, and there is no form of mining or digging in which the element of luck plays such an important part.

Small fortunes have been made in a few days by a new chum, have been in some cases picked up on the surface in the shape of a big and valuable stone, without a pick having been put in the claim; and the adjoining digger may be a man grown hoary at the work, who has never found enough to do more than barely pay for the poorest food—indeed he may be, and often is, half-starved. But in the excitement of a big "find" in the vicinity, such as he are forgotten, and he indeed usually forgets his bad luck himself, buoyed up and encouraged by his neighbour's luck, which will be talked of long after he and the rank and file of unlucky ones have been forgotten.

But to return to the process of sorting. Not only has the digger carefully to watch and regulate every process down to the dumping of the sieve on the sorting table, but in the sorting itself he has to be extremely careful. His eye may be gladdened by the sight of a glittering stone, with its facets as bright as though fresh from the cutter, and fully exposed in the centre of the sieve—a triumph to his art as a gravitator—or it may be that the diamond, if present, is oxidised to such an extent as to be unrecognisable except to the eye of an expert; or it may be a splint or a "mackel," or stone of unsymmetrical shape, and be thrown to the outside of the sieve, instead of being in the centre. The eye, tired with the constant attention of hour after hour of such work, can easily miss such stones as these, or in a moment of inattention they may be swept off the table with a handful of worthless gravel. Should, however, a find be made, the diamond, if at all oxidised, is placed in a bottle of hydrofluoric acid and allowed to remain in it during the night, after which it will be found perfectly clean, though it is often by no means bright, but dull and cloudy, until it has ultimately passed through the hands of the cutter.

(To be continued.)

## NOTE ON AUGITE FROM VESUVIUS AND ETNA.

By HENRY S. WASHINGTON and H. E. MERWIN.

(Concluded from p. 80.)

On such a hypothesis the formation, either simultaneous or successive, of a granular pyroxenite, composed of closely packed and adherent, anhedral crystals, and free-floating, euhedral crystals, is readily understandable; more readily thus, it seems to me, than on a hypothesis based purely on the influence of gravity. It also serves to explain, as that of gravity does not, such examples of vertical, tubular differentiation as those of Magnet Cove and Mount Johnston, Quebec, which are impliedly regarded by Suess as analogous to "piping" in a steel ingot (Suess, "The Face of the Earth," 1909, iv., 559. Cf. H. S. Washington, *Jour. Geol.*, 1901, ix., 607; F. D. Adams, *Jour. Geol.* 1903, xi., 254).

But we are getting far away from our little augite crystals. Let us pass on to those of a near-by volcano, Etna.

*Augite of Monti Rossi, Etna.*

The loose crystals of augite that are found in ɔundance in the ashes and tuffs of Monti Rossi, ɔrmed by the eruption of 1669, and elsewhere round Etna, would seem to have been among the rst augites to be studied. They were described s early as 1783 by Romé de L'Isle, a few years iter by Dolomieu (1788), and by Spallanzani bout 1792. It may be of historic interest to cite ere Spallanzani's analysis, which seems to have een the first, or among the first, of the analyses f these augites (Spallanzani, "Viaggi alle due icilie," (1) chap. vii. (p. 172 of Milan ed., 1825). n a (somewhat pathetic) note referring to the low ımmation he says: "It must be noted that, apart :om the almost unavoidable loss in manipulation, nd that of the moisture present in the schorls, ie lime is here deprived of the acid with which . was originally provided (combined)."). He ɔund: "free silica 34·5, lime 18·7, iron 7·6, lumina 12·4, magnesia 11·0, sum 84·2." It will e seen that, imperfect as the analysis is from the ıodern standpoint, Spallanzani determined the resence of all the most essential constituents, nd approximately in their relative order of bundance.

*Physical characters.*—The augite crystals examined were obtained in July, 1914, by Dr. Day nd me in the ashes of the western summit of Monti Rossi, near Nicolosi. Though they do not ppear to be as abundant as they were in Spallanzani's day, yet a handful was readily collected in alf-an-hour.

The habit is the usual one, like that of the crytals of Vesuvius and Stromboli, though they are, n the whole, somewhat smaller, and with a decidedly greater tendency to prismatic development, some of them being three times as long as hick. They are bounded by the planes $a(100)$, $(010)$, $m(110)$, and $s(\bar{1}11)$. The ordinary contact wins (twinning plane $a(100)$) seem to be rarer han at Vesuvius or Stromboli. They are jet ılack, and the faces are lustrous, much brighter han those of the Vesuvius crystals, though close examination shows that they are not flat planes, ɔut are as if the crystals were cracked, so that hey do not give good reflections for the goniometer. For this reason no crystallographic measırements were made.

In powder or particles under the microscope hey are of a greenish-grey colour, without proıounced pleochroism. The refractive index $\beta$ varied from 1·710 to 1·715; the highest value of was 1·735, and the lowest of $\alpha$ was 1·702. Thus he chemical analysis is probably very closely represented by the values:

$$\alpha=1{\cdot}704,\ \beta=1{\cdot}711,\ \gamma=1{\cdot}732.$$

The extinction angle is high, but was not determined, as the cleavage is poor and it was not thought worth while to grind a section parallel to $b(010)$.

The specific gravity of the crystal fragments used for the analysis, determined with a pycnometer, was 3·373 referred to water at 22°.

*Chemical composition.*—The loose crystals appear to be very pure, except for patches of a siliceous material (which was readily removed by dilute hydrofluoric acid). Small grains of yellow olivine project from the surfaces, but they are not found in the interior of the crystals. After crushing a batch of crystals to small fragments for analysis, all these olivine particles were carefully removed by repeated search under a binocular, and the material used for analysis is confidently believed to have been free from them. The crystals, however, contain a small amount of minute inclusions of magnetite, which it was impracticable to remove entirely. Treatment with a magnet of about 0·6 g. of the powder analysed showed that this was present to the extent of 3·94 per cent and in column 2 of Table II. the anlysis is corrected for 4 per cent of magnetite.

TABLE II.

| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| $SiO_2$ ... ... | 47·80 | 50·09 | 47·63 | 47·38 |
| $Al_2O_3$ ... ... | 3·55 | 3·71 | 0·74 | 5·52 |
| $Fe_2O_3$ .. ... | 4·17 | 1·47 | n.d. | 5·52 |
| $FeO$ ... ... | 5·98 | 4·96 | 11·39 | 7 89 |
| $MgO$ .. ... | 13·40 | 14·01 | 12·90 | 15·26 |
| $CaO$ ... ... | 21·49 | 22·48 | 20·87 | 19·10 |
| $Na_2O$ ... ... | 0·70 | 0·73 | n.d. | n.d. |
| $K_2O$ ... ... | 0·01 | 0·01 | n.d. | n.d. |
| $H_2O+$ ... .. | 0·21 | 0·22 | 0·29 | 0·43 |
| $TiO_2$ ... ... | 2·02 | 2·11 | n.d. | n.d. |
| $MnO$ ... .. | 0·20 | 0·21 | 0·21 | 0·10 |
| | 99·62 | 100·00 | 100·03 | 99·53 |
| Sp. gr. ... ... | 3·373 | | 2·886 | 2·935 |

1. Augite, Monti Rossi, Etna. Washington analyst.
2. Same, corrected for 4 per cent of magnetite.
3. Augite, Monti Rossi, Etna. S van Waltershausen analyst. *Der Etna*, 1880, II, 490.
4. Augite, Monti Rossi, Etna. Rammelsberg analyst. *Pogg. Ann.*, 1858, liii., 436.

Only five or six published analyses of these augites are to be found, and all suffer from the same defects that were pointed out in the case of the Vesuvian augite, that is, non-determination of titanium and alkalies, and, in many, non-separation of the iron oxides.

*Discussion.*—Any extended discussion of my analysis is unnecessary here, and will be reserved for a future occasion, in connection with those of other Italian augites. It may, however, be of interest to give the composition of the Etna augite in terms of the usual molecules, which is as follows (No. 1):—

| | 1 | 2 |
|---|---|---|
| $CaMgSi_2O_6$ ... ... | 70·0 | 80·1 |
| $CaFeSi_2O_6$ ... ... | 16·5 | |
| $CaSiO_3$ ... ... ... | 1·5 | none |
| $(Mg,Fe)SiO_3$ ... ... | none | 7·5 |
| $(Mg,Fe)Al_2SiO_6$ ... | 7·0 | 7·0 |
| $Na(Fe,Al)Si_2O_6$ ... | 5·0 | 5·4 |

It will be seen that the Etna augite (1) is composed very largely of diopside and hedenbergite molecules, with a little wollastonite and acmite, and a small amount of the aluminous Tschermak molecule. In general it much resembles the augite (2) of Stromboli (Kozu and Washington, *Amer. Jour. Sci.*, 1918, xlv.; 468), though this carries somewhat less of the diopside molecule, and considerable hypersthene instead of wollastonite. The respective refractive indices are as follows:—

Augite, Etna $\alpha=1{\cdot}704$, $\beta=1{\cdot}711$, $\gamma=1{\cdot}735$.
Augite, Stromboli, $\alpha=1{\cdot}693$, $\beta=1{\cdot}699$, $\gamma=1{\cdot}719$.

This is not the place to discuss the differences, but it may be mentioned that the higher indices of the Etna augite are to be connected with its higher wollasonite and titanium content, which

seem to more than counter-balance the higher ferrous oxide of the Stromboli augite. The Stromboli augite, furthermore, is slightly higher in magnesia, which would tend to lower the refractive index. On the whole, it may be said that the chemical and optical data for both of these augites are quite in accord, and bear out observations made on the pyroxene molecules generally.—*American Journal of Science* January, 1921.

## BENZYL ALCOHOL FOR TOOTHACHE.*

By DAVID I. MACHT, M.D.

IN 1918, I announced my discovery of the local anesthetic properties of benzyl alcohol, or phen methylol, and published both pharmacologic and clinical data on the subject (D. I. Macht, *Jour. Pharmacol. and Exper. Therap.*, April, 1918, xi., 263). I found that solutions of that drug in concentrations of from 1 to 4 per cent by volume, in physiologic sodium chloride solution or in distilled water, furnished a satisfactory local anesthetic for general surgical work, on the one hand, and that benzyl alcohol was at least forty times less toxic than cocaine, on the other. It was found that solutions of phenmethylol produced efficient anesthesia, especially when infiltrated in the tissues, either alone, or, still better, combined with small doses of epinephrine. On application to mucuous membranes, solutions of benzyl alcohol produced also a distinct anesthetic effect, but the anesthesia is very superficial and does not penetrate into the deeper layers of the tissues. It was found that a much better anesthesia of mucuous or skin surfaces could be produced by application of pure benzyl alcohol. Pure benzyl alcohol cannot be injected into living tissue for the same reason that pure ethyl alcohol cannot be administered in that way; it leads to local necrosis. When applied to mucuous surfaces, however, the drug is not irritating and produces a marked anesthetic effect.

I undertook experiments with a view of enhancing the penetrating power of benzyl alcohol when applied to mucuous or skin surfaces. It was found that when the drug was mixed with certain lipoid solvents, the local anesthesia after its application extended more deeply below the surface. Among the most satisfactory of such solvents were found to be xylene and chloroform, especially the latter.

In the present note I wish to call the attention of the general practitioner to the very satisfactory minor use of benzyl alcohol. I have found, as have others, that benzyl alcohol either alone (100 per cent), or, still better, when mixed with an equal part by volume of chloroform, furnishes a most efficient anodyne for toothache, when introduced on a pledget of cotton into a tooth cavity, or applied to an exposed nerve. The relief obtained by the use of such drops is marked and almost instantaneous, and is also long-lasting. I am not aware of any other drug, with the exception of cocaine, which is more efficient in relieving tootache. As benzyl alcohol is the least toxic of all the well-known local anesthetics, the repeated and free use of such a combination as was described above is free from the objections which are raised by the employment of cocaine, and it can be administered with impunity even to small children. It is for this reason that it was deemed worth while to publish this note in order to advise the medical practitioner of simple remedy for the relief of one of the most excruciating forms of pain.—*American Journal of Pharmacy*, January, 1921.

* Pharmacological Laboratory of the Johns Hopkins University.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

*Ordinary Meeting, February 3, 1921.*

PROF. C. S. SHERRINGTON, President, in the Chair.

THE following papers were read :—

"*The Field of an Electron on Einstein's Theory of Gravitation.*" By G. B. JEFFERY, D.Sc.

The metrical properties of the space surrounding an attracting point mass are given by the line element :—

$$ds^2 = -\gamma^{-1}dr^2 - r^2d\theta^2 - r^2\sin^2\theta d\phi^2 + \gamma c^2dt^2,$$

where $r$, $\theta$, $\phi$ are polar co-ordinates, $c$ is the velocity of light and

$$\gamma = 1 - \frac{2\kappa m}{c^2r}$$

$\kappa$ being the constant of gravitation and $m$ the mass constant of the singularity.

In the case of an electron we have a singularity of both the gravitational and electric fields, and Nordström has shown that the line element is of the same form, but that a new term occurs in $\gamma$—

$$\gamma = 1 - \frac{2\kappa m}{c^2r} + \frac{\kappa \epsilon^2}{c^4r^2}$$

where $\epsilon$ is the charge constant of the singularity. This result is obtained by a different method, and equations are obtained for the motion of a single electron about an atomic nucleus. It appears that the orbits are strictly periodic, with a rotation of the apse line.

If a ray of light passes through the field of the electron, provided that the distance of closest approach is not too small, the ray is deflected towards the electron. For closer approach, however, the sense of the deflection is reversed until in the limit the ray is reflected back again along its original path.

Finally, these results are used to ascertain whether any possible electric field of the sun would produce a measurable effect on the crucial phenomena of Einstein's theory. It is found that, while the sun's electric field would tend to diminish the displacement of the spectrum lines, the field required to produce compensation is of the order of $10^{18}$ volts per cm. at the sun's surface. This value is taken to be far beyond the bounds of possibility.

"*A Physical Theory of Stellar Spectra.*" By M. N. SAHA, D.Sc.

A theory of thermal ionisation (and partly of thermal radiation) of gaseous elements has been developed and applied to the explanation of the ionisation observed in the solar chromosphere, and the absence of certain elements from the Fraunhofer-spectrum. The theory was based upon the

application of Nernst's theorem of the reaction-isochore for chemical equilibria towards the problem of ionisation, which is regarded as a sort of reversible chemical action between the atom, the electron, and the atom which has lost one electron (*e.g.*, $Ca \rightleftarrows Ca^{+} + e - U_1$). The energy of ionisation $U_1$ is calculated from the ionisation-potential, which is deduced either from the convergence frequency of the principal series in the spectra of elements or from the experimental work of Franck, McLennan, and others.

In the present paper, the theory has been extended towards a physical explanation of the ordered gradation in the spectra of stars. The stellar data, particularly those accumulated by Harvard College Observatory, are discussed from the standpoint of the present theory, and it has been shown that the varying spectra of stars can be explained as functions of a single physical variable, viz., the temperature of the stellar atmosphere. To take a typical example, the K-line which is due to $Ca^+$, just appears in the Mb class, marking that Ca-atoms have just begun to be ionised at this stage. The *g*-line which is due to Ca disappears from above the Bg class marking that all calcium has become ionised at this stage and upwards. The K-line of $Ca^+$ disappears at the Od class showing that from above this stage we have neither Ca nor $Ca^+$ atoms but only $Ca^{++}$ . . . atoms. Similar calculations are made for $Mg^+$, Sr, $Sr^+$, He, $He^+$, and H. The temperatures obtained for the different spectral classes are quite concordant and in good agreement with the numbers obtained by H. N. Russell from other considerations.

"*The Ultra-microscopic Structure of Soaps.*" By W. F. DARKE, J. W. MCBAIN, and C. S. SALMON.

1. The ultra-microscopic observations of Zsigmondy and Bachmann have been confirmed, interpreted, and extended. Their observations referred almost entirely to soap curds, not gels or sols, for the latter usually exhibit in the ultra-microscope nothing except Brownian particles, and that only under definite conditions.

2. The cinematograph has been employed as an aid in elucidating the formation and disappearance of the various structures observed.

3. Curds of sodium soap consist of a felt of hydrated fibres enmeshing, and in equilibrium with, a soap gel or gel of definite concentration, the solubility rising rapidly with temperature. The individual fibres may be many cm. long, but they are barely of microscopic diameter.

4. Potassium soap solutions, on cooling, first develop fibres which are similar to those of the sodium soaps, except that they are only a few hundredths of a millimetre in length, and that they have a strong tendency to form twins. The stable condition at room temperature is, however, the formation of innumerable tiny lamellar crystals of hydrated soap.

5. The hydrogen soap, cetyl-sulphonic acid, is similar to the potassium soaps, but the particles of colloidal cetyl-sulphonic acid are very much more prominent.

"*Linear Transformations and Functions of Positive Type.*" By J. MERCER, D.Sc.

The paper contains developments of the theory of linear functional transformations as developed by F. Riesz in his paper, "Untersuchungen über Systeme integrierbaur Funktionen" (*Math. Annalen*, lxix., pp. 449-497) The developments are made with a view to the expansion of a function $\kappa(s, t)$, which is obtained by subjecting a function of positive type, $\gamma(s, t)$, to linear transformations with respect to the variables, in terms of bi-orthogonal and orthogonal systems of functions. The results obtained include as particular cases the expansions of the two symmetrisable functions $\kappa(s, t) = \alpha(s)\,\gamma(s, t)$ and $\kappa(s, t) =$

$$\int_a^b \alpha(s, x)\,\gamma(x, t)\,dx$$

which were given in my communication printed in *Proceedings*, A, xcvii., pp. 401-403.

## SOCIETY OF PUBLIC ANALYSTS.

*Annual General Meeting, February* 2, 1921.

Mr. ALFRED SMETHAM, President, in the Chair.

THE President delivered his Annual Address. The following were elected as Officers and Council for the ensuing year :—

*President*—Alfred Smetham. *Past-Presidents*—Leonard Aichbutt, Edward J. Bevan, A. Chaston Chapman, Bernard Dyer, Otto Hehner, Samuel Rideal, E. W. Voelcker, J. Augustus Voelcker *Vice-Presidents.*—W. J. A. Butterfield, C. A. Keane, G. Rudd Thompson. *Hon. Treasurer*—Edward Hinks. *Hon. Secretaries*—P. A. Ellis Richards, E. Richards Bolton. *Other Members of Council.*—F. W. F. Arnaud, B. A. Burrell, F. H. Carr, R. L. Collett, C. H. Cribb, Norman Evers, P. J. Fryer, J. H. B. Jenkins, S. E. Melling, G. W. Monier-Williams, Raymond Ross, C. J. H. Stock.

*Ordinary Meeting, February* 2, 1921.

Certificates were read for the first time in favour of Messrs. Jules-Cofman-Nicoresti, Walter K. Fletcher, William Singleton, Francis G. H. Tate, James Darnell Granger, Ph.D., F.I.C., Russell G. Pelly, F.I.C., Ed. B. Maxted, Ph.D. (Berlin), B.Sc. A certificate was read for the second time in favour of Mr. W. R. Schoeller, Ph.D. The following were elected Members of the Society: Messrs. Urban Aspey, Herbert Corner Reynard, B.Sc. (Lond.), A.I.C., Edwin Burnhope Hughes, B.Sc., (Lond.), A.I.C., Harry Jephcott, M.Sc. (Lond.), A.I.C., Arnold Lees, A.I.C.

The following papers were read :—

"*Iodimetric Determination of the Diastatic Power of Malts.*" By J. L BAKER, F.I.C. and H. F. E. Hulton, F.I.C. The authors make use of the quantitative oxidation of maltose to maltobionic acid by means of iodine in the presence of sodium hydroxide, and details for working the estimation are given, together with results obtained on the same samples by this and the Ling methods. The advantages claimed for this method are the greater accuracy with which the iodine titration may be carried out as compared with Fehling's solution, the elimination of an external indicator, and the possibility of using artificial light for the final titration.

"*Extract of Red Squill* (*Scilla maritama*) *as a Rat Poison*." By F. W. Smith, B.Sc., A.I.C. After considerable practical experiment with different preparations of various types of squills, the author found that the most effective form of squill rat poison was that prepared in water from an alcoholic extract of the fresh bulb of the red squill (*scilla maritama*), and that salicylic acid may be used as a preservative without fear of hydrolysing the glucoside.

"*The Composition of Harrogate Mineral Waters*." By William Lowson. The author gives a summary of the analyses carried out in connection with Prof. Smithell's recent general survey of the Harrogate mineral waters, and for comparison a table of analyses dating back some ninety years.

## NOTES.

Sir John Cass Technical Institute.—The Annual Prize Distribution was held on Thursday, February 10, when the prizes were distributed by Sir Frederick Black, K.C.B., who subsequently delivered an address on "Liquid Fuel in Peace and War." The Chairman of the Governing Body, the Rev. J. F. Marr, in giving a summary of the work of the Institute during the past session, stated that the total number of students was 1060, a higher figure than in any previous year, and an increase of over 50 per cent on the previous session. An important development of their work they hoped to be able to realise shortly was the initiation of courses of instruction on petroleum technology, adapted to the needs of those already engaged in the industry. They had received very helpful encouragement in connection with this project from representative members of the industry, and it was considered that the Institute was exceptionally well situated for the development of this branch of applied science. In the course of his address, Sir Frederick Black said that whilst the United Kingdom had become an important consuming centre of petroleum products, it was at present only on a comparatively small scale that petroleum, either natural or derived from shale or coal was produced in this country. So far as manufacture or refining was concerned, much more work of that nature was likely to be undertaken at home, and it was probable that home production would also increase. Large British companies interested in oil had their headquarters and distributing agencies here though their wells and refineries were mostly situated in distant countries. The scientific and technical training of men for oil work, geological, chemical, and engineering was already undertaken at such centres as Birmingham University and the Imperial College of Science at South Kensington in particular, where complete courses of instruction were given, similar to those in the mining profession. The Sir John Cass Institute, whilst not expecting to compete with such centres, hoped very shortly to arrange courses of lectures for some of the staff of the oil companies, which should aid them in the efficient discharge of their duties. The Governing Body had prepared a scheme, modest to begin with, but capable of extension, and some of the large oil companies were assisting in working out the scheme and were favourably disposed towards practical help in the cost involved. After briefly describing how the products of petroleum used for fuel were obtained, Sir Frederick proceeded to give a general description of their use in internal combustion engines and for steam raising. If the war had not absolutely discovered any entirely new application of petroleum products, it had enormously developed their use and established their importance on land and sea and in the air. He touched upon the relative advantages of oil and coal for marine purposes, and the methods of handling, and made special reference to the progress in the building of motor-driven ships since the arrival of the "Selandia" in the Thames in 1912 created so much interest. Great attention was being given, not only to the opening up of new sources of supply, but to such important matters as the elimination of waste on the oil fields and in the use of liquid fuels. Oils that admitted of complete refining into such products as motor spirit, lighting and lubricating oils should be so dealt with, in preference to burning the more valuable fractions for steam raising, if a heavier oil not capable of such complete refining could be made available. He hoped that the new work to be undertaken in the Sir John Cass Institute would not be without useful result in respect of some at least of these problems.

The General Report on the Industrial and Economic Situation in Germany in December, 1920, recently issued by the Department of Overseas Trade, was sold out within a few days of publication. A further edition has been printed and the Report (Cmd. 1114) can be obtained, price 9d. (post free 10½d.) on application to H.M. Stationery Office, at the following addresses: Imperial House, Kingsway, London, W.C.2; 28, Abingdon Street, London, S.W.1; 37, Peter Street, Manchester; 1, St. Andrew's Crescent, Cardiff; 23, Forth Street, Edinburgh; or from E. Ponsonby, Ltd., 116, Grafton Street, Dublin.

Under the title "Famous Chemists: the Men and their Work," Messrs. George Routledge & Sons, Ltd., will shortly issue a new work by Sir William Tilden, F.R.S. The volume contains an account of the lives of 21 of the most famous discoverers in chemistry from Robert Boyle to Sir William Ramsay, and will be liberally illustrated. The selection of names has been made in accordance with a definite scheme which is explained in the preface, and the treatment is chiefly biographical. Information has been derived from original sources, some of which have not hitherto been accessible to the English reader. An attempt has been made to give not only a picture of the men and their achievements but also to trace the social and political conditions of the times in which they lived, so as to show something of the relation of discovery in physical science to the progress of civilisation. As it will be entirely free from technicalities, it is hoped that the volume will be acceptable not only to scientific people, but generally to the reading public.

TO DETECT THE PRESENCE OF MOLYBDENE.—Some crystals of xanthogenate of potassium and a few drops of strong acid are added to the neutral cold solution. There is then a yellowish colour from free xanthogenic acid, followed by red and violet. With small quantities of molybdene the colour is red. With large quantities of molybdene, black oily drops are precipitated. Heat prevents re-action. The reagent can be made with a mixture of carbon sulphide and alcoholic potash, but the solid commercial product keeps well. The coloured product is soluble in ether, amyl acetate and chloroform. It is preferable to eliminate the salts of Cu, Co, Ni, of ferric iron, of hexavalent Ur, although the colouration they give is very much less than that from molybdene. $Va_2$, Os, $UO_3$, $WO_3$, do not impede reaction. Oxalic acid does. Thus 5/1000 of a mgrm. of Mo can be detected. *Chimie et Industrie*, November, 1920.

ALSACE.—In a very exhaustive report, M. de Retz, technical director-general of the potash mines under sequestration, estimates at 14,000 metric tons of potash salts per diem the tonnage which can be supplied daily in four or five years by the 17 shafts now being sunk in the Mulhouse basin, if the growth of the staff follows development of the plant. An annual production of four million tons of sylvinite with 700,000 tons of pure potash would thus be obtained, but the area of the prospected deposits will permit of a greater production, and there is no doubt that grantees will not hesitate to sink new shafts.—*L'Engrais.*

ANALYSIS OF AMMONIACAL NITROGEN IN FERTILISERS.—Calcic cyanamide is usually classed amongst ammoniacal fertilisers. From the agricultural point of view this is admissible, but not from that of the commercial. In a humid atmosphere cyanamide quickly changes, and then contains a large quantity of dicyanamidic nitrogen, and it has been noted that dicyanamide clearly delays nitrification of the ammonia from calcic cyanamide. It is therefore desirable that the percentage of dicyanamide in this product should be as little as possible, and it is necessary to be able to analyse the percentage of ammonia in a complex fertiliser with a base of calcic cyanamide and ammoniacal salts. According to Messrs. Froidevant and Vandenberghe (*Chimie et Industries*, November, 1920) the ordinary process based on distillation in presence of magnesia is not applicable in this case. They describe another method employed with success, based upon the action exerted by a cold concentrated soda lye and subsequent disengagement of ammonia. The apparatus consists of a stoppered bottle, 125 cubic cm. in capacity, placed in a crystalliser. There are three necks in the bottle through which a tube runs to the bottom and communicates at the higher part with a washing bottle containing an aqueous sulphuric acid solution to absorb atmospheric ammonia. A tube in the second neck is furnished with a cock to introduce the soda lye. The third tube is bent twice and 30 cm. high. The last tube is to retain projections of alkaline solution during passage of air.

## New Patents.

THIS List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

3848—Briscoe, H. V. A.—Separating solids by crystallization from solvents. Feb. 1st.
3742—Duclaux, J.—Treatment of esters. Feb. 1st.
4100—Lindsay Light Co.—Manufacture of thorium compounds. Feb. 3rd.
3949—Soc. l'Air Liquide.—Synthesis of ammonia. Feb. 2nd.

*Specification published this Week.*

158130—Davis, C. T.—Imperviously covered solid or tablet pharmaceutical or chemical preparation.
141758—Soc. l'Air Liquide.—Processes for the production of hydrogen peroxide.

*Abstract Published this Week.*

*Bichromates.*—Mr. R. L. Datta of Calcutta, India, has recently obtained a Patent No. 154810 in this country for an improved method of obtaining bichromates. Sodium and potassium chromates are converted into their respective bichromates by the addition of the corresponding acid sulphate. For example, by adding sufficient potassium hydrogen sulphate in the form of a coarse powder to the hot solution of potassium chromate, all the latter is converted into potassium bichromate. After filtering, the solution is concentrated, when potassium sulphate separates. From the mother liquor after all sulphate is removed, potassium bichromate is obtained by crystallization.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

## MEETINGS FOR THE WEEK.

*Monday, February 28.*

Royal Society of Arts, 8.

*Tuesday, March 1.*

Royal Institution, 3. "Darwin's Theory of Man's Origin" by Prof. Arthur Keith.
Institute of Chemistry. (Annual Meeting).
Röntgen Society, 8.15.

*Wednesday, March 2.*

Society of Public Analysts, 8. "Acidity of Ink and the action of Bottle Glass on Ink" by C. Ainsworth Mitchell. "Detection of Adulteration in Butter by means of the Melting-Point of the Insoluble Volatile Acids" by George Van B. Gilmour. "Method and Appartus for Routine Determination of Melting Points of Fats and Fatty Acids" by S. H. Blichfeldt and T. Thornley.
Royal Society of Arts, 4.30.

*Thursday, March 3.*

Royal Society, 4.30. Discussion on "Isotopes," opened by Sir J. J. Thomson. The following also will probably speak:—Mr. F. W. Aston, Prof. F. Soddy, Prof. T. R. Merton and Prof. F. A. Lindemann.
Royal Institution, 3. "Mason Wasps" by F Balfour Browne.
Chemical Society, 8.

*Friday, March 4.*

Royal Institution, 9. "Severn Crossings and Tidal Power" by W. A. Tait.
Royal Society of Arts, 8.
Society of Chemical Industry. (At Manchester and Cardiff).

*Saturday, March 5.*

Royal Institution, 3. "Electricity and Matter" by Sir Ernes Rutherford.

THE CHEMICAL NEWS.
VOL. CXXII., No. 3177.

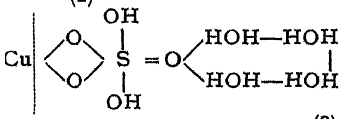
## THE THEORY OF AUXILIARY VALENCIES AND "WATER OF CRYSTALLISATION."

By H. T. F. RHODES.

(Continued from p. 87.)

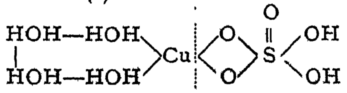
IT is necessary, before proceeding directly to 'Conclusions," to make allusion to a paper which had escaped the present author's notice until the time of writing this second part (see J. Macleod Brown, CHEMICAL NEWS, cix., No. 2833, p. 123). The paper credits copper with quadrivalency, or oxygen with a like valency, and assigns to the quinquehydrate of copper sulphate the structure:

(1)

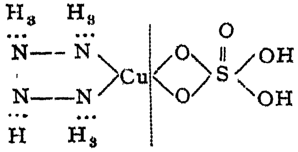


or

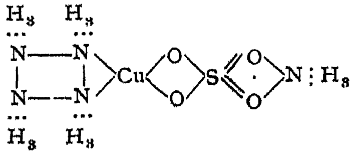
(2)



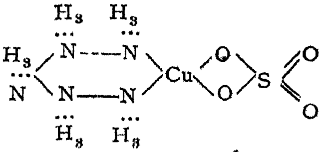
The paper favours formula 2, since in this case the copper ion is more evenly balanced. Formula 1 is substantially in agreement with the author's conclusions except that oxygen is definitely made quadrivalent; a conclusion which is certainly allowable and even probable. The paper, however, claims for formula 2 an analogy with quadrammine cupric sulphate to which has been assigned the structure:—



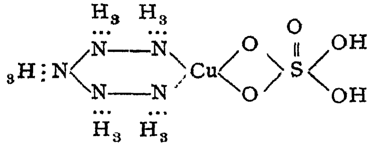
Here a difficulty presents itself, since granting this, to quinqamm'ne cupric sulphate, the following structure must be assigned:—



There is no evidence to support the view that one ammine group is separate from the others; and indeed, its method of hydroxyl substitution step by step is opposed to the idea. Again it will be obvious that if the formula

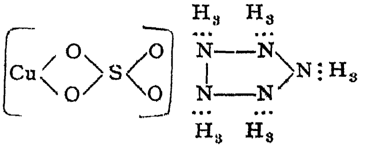


be assumed, a compound of the formula

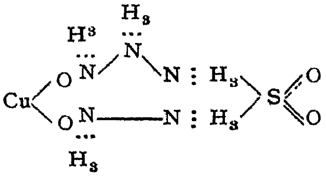


should exist; and no such compound is known. This would seem to be a fair statement of the case for the quadrivalency of copper which, it must be admitted, is not strong.

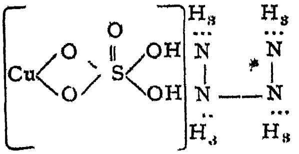
The assumption that the copper atom is mechanically retained within a ring of five $NH_3$ groups is open to the same objection. It seems necessary to assume, therefore, by a process of climiniation, the structure:—



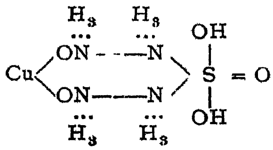
or



That assumes molecular affinity or the quadrivalency of oxygen. Upon this supposition $Cu(NH_3)_4SO_4.H_2O$, becomes:—



or



which is analogous to Formula 1 and $\beta$-indirect but strong evidence (if analogy is in this case to be allowed) in favour of these structures either of which would seem to be compatible with the behaviour of the salt on ionisation.

### *Conclusions.*

Werner, by his assumption that the chlorine atom in ammonium chloride was mechanically attached to the nucleus seems to agree with the principle of the earlier theory of Kekulé.

Kekulés theory at least possesses the advantage of simplicity, a simplicity that was destroyed when the term "auxiliary valency" came to be employed, for it has proved increasingly difficult to distinguish between the two kinds of affinity, and now, therefore, it is necessary to assume either that valency must suffice for all, or that recourse must again be had to some theory free of those definitions by which Kekulé's theory has been paralysed.

The disadvantage to Kekulé's hypothesis lies not so much in the theory itself as to its attempted application to compounds that are more easily explained by the law of valency. The application of such a theory to water of crystallisation is reasonable, but its application to ammonium chloride—since nitrogen is known to be quinquevalent in some cases—is unnecessary and absurd The fact that ammonium chloride begins to dissociate at 350° C. does little or nothing to support such a contention; nor can it be adduced as evidence in favour of instability. (It is impossible to judge ammonium salts by a standard to which they are unqualified to conform. It is perhaps undesirable to regard them as "stable" or "unstable," but for our purposes an analogy could justly be sought in such a compound as ($SO_2Cl_2$). In this sense the ammonium salts are extremely stable. Nor must it be forgotten that at least 15 per cent of ammonium chloride remains undissociated at 1000° C., and that sulphuric acid completely dissociates at 450° C.).

The difficulty of Kekule's theory lay in the fact that it requires the assumption that the affinity increases as the number atoms, and this, of course, is not the case, but by combining it with the heterocyclic theory of valency this difficulty disappears.

At the same time it has to be admitted that in some cases the stability appears to increase as the complexity: the alums are an example:

| | M.P. |
|---|---|
| $Al_2(SO_4)_3(NH_4)_2SO_4.24H_2O$ | 200° |
| $Fe_2(SO_4)_3(NH_4)_2SO_4.24H_2O$ | 230° |
| $Rh_2(SO_4)_3(NH_4)_2SO_4.24H_2O$ | 110° |

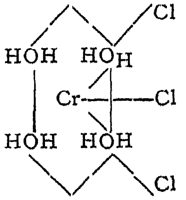
This is admittedly a difficult question and no satisfactory explanation can readily be found. The "gravitational" theory holds, but this increased stability is not true of all salts. The assumption, on the other hand, that in the alums this affinity and true valency operate together is not convincing, and is further open to the objection that if the two forms of affinity operate in one case there is no good reason why they should not operate in all. But it seems necessary to assume that some additional force is at work in these cases, and beyond this little can be said.

Space forbids a detailed discussion of a supposed molecular property whose principal claim for consideration lies in the fact that it cannot be confused with valency; but the point that no dogmatic statement is made with regard to it, cannot be too strongly emphasised. It is merely a trial hypothesis that is convenient in its application to some compounds whose powers of valency are doubtful; and if an alternative be necessary, some such theory as that which has been outlined seems advisable in order that confusion may be avoided.

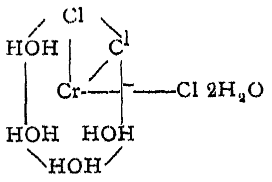
It is desirable to add some remarks with regard to those hydrates which have already been discussed.

$X.6H_2O$.—It has been assumed in the case of magnesium sulphate that the metallic atom is mechanically retained within the ring; so that the interesting question presents itself as to whether it is justifiable to regard the water as being in chemical combination with the salt; and in this case it cannot be denied that the combination is mechanical. But if this general structure is to be allowed, it will not hold for all cases, since two modifications of chromium chloride are known to exist. These can be explained by the inclusion within the ring of chlorine.

*α* form

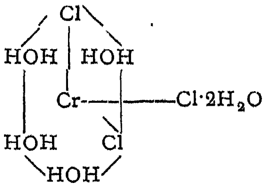


*β* forms

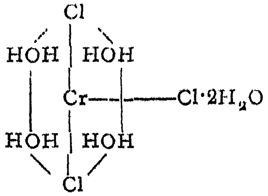


Ortho

*β* forms



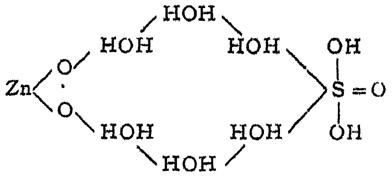
Meta



Para

In the alpha form all the chlorine can be removed by piptation, while in the beta variety but a third. Theoretically three isomers of the beta form are possible, but this does not mean, of course, that they can be isolated. It is known, however, that the alpha salt passes into the beta form when the temperature is elevated, which seems to suggest that the latter is more stable; the formulæ assigned suggest this.

There remains an alternative for those salts that contain seven molecules of water, thus:



If the molecular affinity be disallowed this structure, by analogy with the ammines, seems not improbable. No retardation of the metallic ion appears to have been noticed in the case of zinc or copper; and indeed, Kohlrauch alludes only to the salts of sodium, lithium, barium, and potassium. This question as to the position of the ring is one of interest, and some experimental work is now in progress with a view to arriving at some conclusion with regard to the matter.

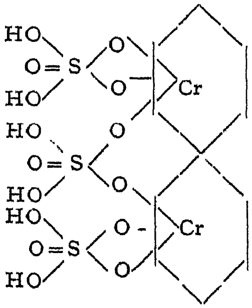
Ephraim and Bolle (*Ber.*, 1915, xlviii, 1770, 1777) appear to have arrived at the conclusion that the stability of some ammines depends not only upon the metal, but also upon the acid group, and their conclusions seem indirectly to support the structure assigned above. This does not mean, of course, that no other conclusion is possible; and, in fact, the explanation advanced by these investigators is different.

Baker (*Proc. Chem. Soc.*, 1909, p. 223) has also assumed that in the case of the ammine that a chain of ammonia molecules divides the anion and cation. Allusion is also made to possible isomerism, apparently of a tautomeric nature, but exactly what is meant does not appear to the present author satisfactorily to emerge.

$X5H_2O$.—These salts have already been fully liscussed and further allusion to them seems to )e unnecessary.

Bihydrates and terhydrates seem to call for no )articular comment, and since there seems no eason for doubting the tervalency of chlorine ınder some circumstances, the structure assigned s open to no objection.

$X15.H_2O$.—It may here be observed that upon he assumption of a double ring, at least the "ic" sulphates which contain this proportion of water :an be classified :—



*Conclusion.*

No apology is necessary for the ring structure of water, since it has already been advanced, and has at least met with sufficient popularity to be included in some text-books. Its application to those salts that contain six molecules of water seems natural, and it would certainly be difficult to find a more satisfactory explanation; but granting the ring structure in general, the question of "within" and "without" the ring is of great importance It is probable the position of the ring varies with different salts, but since the aim of this paper has been only the discussion of some general principles, this aspect of the question has not been elaborated, and will ultimately be made the subject of another paper.

The author cannot close without his acknowledgments to those chemists whose papers have been mentioned, and in particular to the excellent paper of Dr. Friend.

## CUPROUS OXIDES BY REDUCTION.

By V. V. SARMA.

Cuprous oxide is usually prepared by reduction of an aqueous solution of alkaline cupric salt with glucose. In this process the yellow powder that is first formed, rapidly changes into red cuprous oxide. Yellow cuprous oxide is also precipitated when an alkaline hydroxide is added to a solution of cuprous chloride in hydrochloric acid; but the same transformation into the red variety is effected at once if the solution is hot.

Reference to previous literature shows that the best method for preparing yellow cuprous oxide is by reduction of a cupric salt by means of hydroxylamine in presence of alkali. Also when a copper salt is reduced by Fehling's solution, the character of the precipitated cuprous oxide depends on the proportion of tartrate solution used. With excess of tartrate, red crystalline cuprous oxide is formed, and with little tartrate the cuprous oxide is yellow and amorphous (*J.C.S.*, 1919, Abstracts ii., p. 155).

An attempt was made to prepare yellow cuprous oxide by the ordinary method of reduction of a cupric salt with glucose in presence of an alkali. The reduction was effected at the room temperature, in all cases 25° to 30° C. If the glucose solution is added after the addition of alkali to the solution of the cupric salt, the colour of the precipitated oxide will range from orange to brick-red according to temperature. If the reduction takes place in hot solutions, brick-red precipitates is at once formed. At the room temperature transformation into the red variety takes place slowly.

A slight modification, however, in the method of reduction will produce the yellow oxide. If the glucose solution is first stirred into the cupric salt solution and then the mixture made alkaline with sodium or potassium hydroxide, a rich yellow precipitate without the least tinge of red colour is formed in a short time. Once formed, the yellow cuprous oxide is very stable; the solution may be heated to boiling and the dry substance may be heated to nearly 150° C. without loss of colour.

*Experimental.*

The yellow precipitate was washed with cold water, dried at 110° C, and percentage of copper determined by (1) oxidation to cupric oxide, and (2) reduction to copper in a current of hydrogen. In (1) 0·6853 grm. of the yellow powder gave 0·7033 grm. of black cupric oxide. This gives 82·02 per cent. of copper in the yellow oxide 0·6322 grm. of the black oxide obtained above gave, on reduction with hydrogen, 0·5062 grm. of copper corresponding to 80·05 per cent of copper, and showing that the yellow powder was completely oxidised to black cupric oxide.

In (2), 0·4736 grm of the yellow oxide gave, on reduction with hydrogen, 0·3916 grm. of copper, which corresponds to 82·69 per cent of copper in the original substance.

In another experiment the dried yellow product was repeatedly shaken with ether until no change was observed. The ether was removed, and, afte drying, the substance was gently heated out of contact with air until it became completely red. 0·4214 grm. of this red oxide gave, after reduction with hydrogen, 0·3728 grm. of copper, corresponding to 88·45 per cent of copper, and showing that the red substance formed is almost pure cuprous oxide.

*Conclusion.*

The yellow substance formed by reduction of an alkaline cupric salt with glucose does not seem to be pure cuprous oxide. It appears to contain an appreciable amount of cuprous hydroxide which persists even after heating the substance to 110° C. That the yellow substance contains another compound of copper in addition to cuprous oxide is shown by its behaviour towards some common reagents On boiling it with water, a small portion of it remains suspended in water after the boiling is discontinued, while most of it settles down as a granular powder. The heavier portion is not so bright in colour as the lighter one, and when to this suspended portion a drop or two of dilute sulphuric acid is added, a clear and colourless solution is formed. On adding ammonia, the solution remains colourless but becomes blue on standing, showing that ammoniacal cuprous salt was at first formed. On

adding dilute sulphuric acid to the heavier substance, it behaves in the same way as red cuprous oxide, giving a solution of cupric sulphate and copper.

When the yellow powder is shaken with ether, a small portion of it dissolves in ether, and gives a bluish-green solution. The substance that remains loses its brightness, and becomes dull yellow in colour. When it is gently heated in a test-tube, a thin green coating is formed on the cooler portions of the tube—evidently a portion of the substance that dissolved in ether—and red cuprous oxide remains behind. Ether has no action on red cuprous oxide.

The characteristic behaviour of the yellow oxide indicates that in addition to the 2 to 3 per cent of water that the dried product may contain (*J.C.S.*, 1919, Abstracts ii.), it is mixed with an appreciable amount of cuprous hydroxide. Also conditions of formation being favourable, yellow cuprous oxide is as stable as the red variety up to a pretty high temperature.

*Note.*—If cane sugar is used instead of glucose, only red cuprous oxide is formed, irrespective of temperature and method of reduction.

Government College Laboratory,
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January 15, 1921.

## THE ALLUVIAL DIAMONDIFEROUS DEPOSITS OF SOUTH AND SOUTH-WEST AFRICA.*

By FRED. C. CORNELL, O.B.E.

(Continued from p. 90.)

The digger is bound to keep a register of all diamonds found by him. He can sell them to a licensed diamond buyer on the spot, or may obtain a permit to export them and sell them overseas, or he may obtain a license to hold them himself. He cannot even give them away without a permit, and in such cases the recipent must also obtain a licence to hold them.

But the digger is usually an impecunious being, and his finds are generally sold to a licensed diamond buyer on the spot. The buyers, as a rule, attend the principal diggings periodically, and their advent is generally signalled by the hoisting of a flag at the local hotel, or some such prominent rendezvous.

Here, rooms are set apart for their use, each individual buyer occupying a separate office, where the prospective seller may interview him in privacy. In some of the centres, a row of tiny huts, about the size of bathing boxes, and each well apart from its neighbour, serves the purpose of the visiting buyers, and on their arrival—usually in a body in motor cars—each little hut flies the pennant of some well-known dealer. And the digger can take his choice; he may, if he chooses, go from one to another and try to obtain a better price for his treasure trove than the first dealer has offered him, but as a rule, so good a judge is the average buyer, and so fair is the price he offers, that little good is done by chaffering. And the regular digger soon becomes a customer of one particular firm of buyers. Of course there are exceptional cases, when extraordinarily fine stones have been found, or when the digger—as is occasionally the case—puts a fictitious value upon his hard-earned find. Or, again, there are cases when the buyer is anxious for a particular variety of stone to make up a parcel for Hatton Garden, and when he will pay an exceptional price for the class of stone he needs.

Of course all stones are weighed minutely, as a rule not only by the buyer, but by the digger himself; then again not only size, but colour, shape, and purity are factors in the value of the gems.

With the exception of so-called "fancy" stones, which are stones of a pronounced colour, and are very rare, the most highly-priced diamond is the so-called "blue-white"; a white stone of exceptional purity and with a suggestion of blue in its brilliant and liquid scintillescence. But these are seldom met with, and the digger is well content if his find is of the pure and colourless variety, known as the "Cape White." Many of the larger stones are slightly brownish or yellowish in tint, and these do not command the price of the white stones; though a brilliant canary yellow or an orange coloured stone would command a very high price, as a fancy stone.

The price of diamonds has naturally fluctuated considerably during the long life of the diggings: some twelve years since it was at its lowest ebb, and diggers could hardly dispose of their finds. During this period of depression small white stones of good quality only fetched about 25s. per carat, and the usual poverty of the diggings became terribly accentuated.

To-day, in common with every commodity, the price has gone up, and the same class of stone fetches about £5 or £6 per carat. Against this increase in price, however, there is, of course, the increased price of labour, etc. In addition, a Government tax of 10 per cent. has been levied upon all stones registered; and this impost has hit the digger very hard. In the early days of the diggings, the digger was usually either an old gold prospector from any of the ends of the earth, or one of Kipling's "Legion that never was Listed," a younger son who had been sent out to the Colonies either to "make good" or disappear. Often, as far as the home folks were concerned, he did the latter, reappearing under an entirely different name on the diggings. There are some classical instances of this metamorphosis of young ne'er-do-wells of England, who, partly by luck on the diggings, and partly by push, have become magnates, plutocrats, and even Empire builders, in the country of their adoption. But the average digger has remained a poor man, indeed a very poor man. The possibilities open to the first-comers have long since disappeared. To-day, and indeed from the date of the amalgamation of the mines, his lot has been that of a labourer, a picker up of unconsidered trifles. In sight of him are the mineheads of De Beers, and though he may in his scramble for the crumbs that fall from the rich man's table, occasionally pick up not a crumb, but a plum, his chance of doing so is remote.

Then, again, there is usually a tendency amongst diggers who have struck a rich patch whilst working with a modest gang, immediately to launch out on a larger scale; and expensive machinery and a long wages bill often coincide with bad luck and a long blank, and the embryo "Diamond King" has to sell out at a ruinous cost and begin at the bottom again.

Another favourite ambition of the digger is to try his luck in the actual bed of the present river, which has been found in places to be extremely rich in diamonds. This can only be effected in the dry season when the river is at its lowest. Usually small syndicates are formed by a few of the lucky ones, who have made a little money, and as the river begins to fall, dams, or "breakwaters," as they are termed, are pushed out from the banks to enclose the chosen "pot-hole." This work is expensive, and has, to be carried out rapidly, and often before it can be completed, a sudden flood from late rains up-country may have swept it away. Should, however, the enclosure be completed, the water is pumped out, and work carried on in the mud and ooze of the actual bed. Work of this description is not only unpleasant, but often dangerous, as the river sometimes rises very rapidly, and in the attempt to save valuable machinery and gear from a rising flood, diggers and their natives have often been swept away and drowned. Still it is only fair to add that many of these "pot-holes" have proved extremely rich, and there are not a few successful men on the diggings who have taken ten or even twenty thousand pounds' worth of stones out of a "breakwater" in the river bed during the few weeks the river has allowed them to work.

There are other methods of working the gravel besides those I have described, for instance, in places a very deep deposit on a rise may be quarried, or "open-faced," as it is termed, and the face thus exposed will often show a number of distinct strata of gravel, apparently deposited at different periods by recurring floods, or by the frequent changing of the river's course in the remote past.

Occasionally these deeper deposits are worked by means of shafts and drives, and the operation is then in the nature of mining.

As the result of good finds in "deep ground" of this nature, or where a very heavy deposit of gravel has been proved over a large area, small companies have from time to time been formed to work the gravel on a large scale; but few of these have been successful, and abandoned buildings, and rusted machinery and gear, can be seen in or near most of the diggings of to-day, a melancholy proof that the Vaal River diggings are a poor man's proposition, and never likely to pay dividends on a large capital. Better luck has attended the large companies such as the New Vaal River Company, the Pniel Company, and others which have taken over very large areas of alluvial, and who sub-let claims to the digger, receiving a certain royalty on all finds. Certain of these companies have large pumping stations of their own, whence the water is conveyed in pipes to parts of the diggings remote from the river, doing away with the laborious process of "riding" water to the claims, which has to be resorted to on the ordinary Government ground.

Up to the outbreak of the war the population of the River Diggings had fluctuated between some 3,000 and 5,000 whites, and about three times that number of coloured men, but since the war, and the opening up of new fields, there has been an enormous influx of new diggers, many of them returned soldiers; indeed, in some cases Government assistance has been given to enable discharged men to make a start at this most precarious of livelihoods. The population is an ever-varying one, men out of employment staking their last few pounds on this gigantic "wheel of fortune," men who have come to try their luck for a week or two, and have remained a life-time, many indeed who have never had luck enough to enable them to get away! And in addition whole families of the "poor white" type, men, women, and children, uneducated, uncouth, and miserably poor, all engaged in the search for diamonds. Unfortunately, poor as is the general luck, the life is a fascinating one, and the saying "Once a digger, always a digger," is a very true one. For men who have had hard luck for years, even if they strike it rich at last, seldom go away; or if they do, drift back again in a very short time. Indeed, the life unfits a man for any other occupation.

In the foregoing description of the diggings I have chosen those of the Vaal River as being the more extensive and better known, and fairly typical of all the others.

There are several smaller alluvial diggings, in the vicinity of the Premier Mine, north of Pretoria, at Mahura Muthla, near Kuruman, on the Harts River near Taungs, and notably on the Orange River near Aliwal North.

Those at Rouxville, near the latter place, have recently produced very fine diamonds, but the principal deposits there are in the hands of a company, and do not call for description here. Suffice to say that the company in question has been a success so far, and has proved that in spite of the failure of similar concerns on the River diggings to which I have alluded, under certain conditions a company or syndicate has a better chance than the individual digger.

Diamonds have also been found near the Orange River at several places down stream, below its juncture with the Vaal, and it may well be that the diggings will eventually spread in this direction. Indeed, at the little known lower portion of this river, which near its mouth runs through an extremely wild and mountainous country, and where it forms the boundary between Little Namaqualand, Cape Province, and the newly acquired territory recently known as German South-West Africa, there exist colossal terraces consisting of gravels identical with those of the diggings, but very much more highly concentrated. At a spot about fifty miles from the sea, where the river emerges from a series of narrow cañons which has penned it in for some hundreds of miles, and reaches open country again, these terraces have culminated in veritable hills, two or three hundred feet in height, and consisiting of layer after layer of wonderful gravel.

Here the lower strata have become practically a conglomerate bound together with lime, presenting a precisely similar appearance to the very rich deposit recently found at Rouxville, fully 800 miles upstream and almost at the opposite side of South Africa.

At these huge beds diamonds have been picked up by the natives, but owing to their remoteness and difficulty of access, very little real attempt has been made to test them. Still, owing to the wonderful concentration, these deposits may very possibly some day prove a new and extremely rich source of the diamond.

I have laid particular stress upon these gravels, as they appear to form a connecting link with the diamondiferous deposits upstream, and those of the recently-discovered deposits on the coast of what was recently German South-West Africa.

These deposits were first discovered in 1907, when the sands of Luderitzbucht, a little desolate seaport on the coast north of the mouth of the Orange were found to be full of small glittering diamonds. At first the story was scoffed at, for there had been a German settlement there since 1884, and no one had ever heard or dreamed of diamonds being there. But diamonds they proved to be, and the deposit at Kolmans Kop, quite close to the settlement of Luderitzbucht, soon proved to be but one of many, indeed they have been proved to exist in varying quantities practically all up the coast from a little north of the Orange River well nigh to Walfish Bay.

The whole coast is a dreary and desolate one, bare sand dunes stretching for many miles inland; it is waterless, and with the exception of Luderitzbucht, was, at the time of the discovery, quite uninhabited—indeed, uninhabitable!

The diamonds, which are very small, and very brilliantly polished by the constant blowing sand, are found in a surface deposit of sand and grit. They are so uniform in size as to give the impression of having been graded, as indeed they apparently have, by the action of both wind and water. And though the main deposits have been found at some small distance inland, rather than on the present beach, there is evidence that the coast line has been gradually rising, and that they came from the sea.

Farther transportation has been effected by the prevailing wind, which blows with great force during most of the year, and is the cause of the shifting sand dunes, which are a feature of the country, and which blows pebbles, grit, sand, and even diamonds impartially.

Of the many deposits located, by far the richest is at Pomona, south of Luderitzbucht, where the lucky first-comers literally filled their pockets with little diamonds. And everywhere along the coast, in close proximity to the diamonds, are found pebbles identical with those of the River Diggings I have described, smaller, it is true, but having undoubtedly a common origin.

And the theory, held by many geologists, is that the diamonds were, in common with gravel, at one time washed down the Orange and into the sea, whence the north-east setting currents have borne them along the coast, and the tides have deposited them where they are found to-day. Another theory is that they have been washed up from a pipe in the sea, but this would not account for the gravel, and it is also a fact worth noting, that the size of the stones is larger near the southern extremity of the fields, near the Orange River, and becomes smaller and smaller at each successive field as one journeys north.

In any case, and whatever their origin, their discovery proved a godsend to the German Administration of the country, which had been a drain upon the Imperial German Government. Rules and regulations were hurriedly framed to control the new source of wealth, prospectors and would-be diggers flocked to Luderitzbucht, where at that time a condensing plant had to supply the only driking water, except that obtained from the ships, and where conditions were as unfavourable either for prospecting or digging as can well be imagined.

In spite of this, and at risk of their lives, men spread up and down the coast, and extraordinary finds were made—many of them to be confiscated by the German officials; and within a month or so of the first finds, the Deutscher Bank in Luderitzbucht had an enamelled bucket three parts full of the precious stones, which had been placed in their keeping pending a decision as to the rightful owners.

To add to the general confusion many claimants for certain valuable portions of the coast now put in an appearance, their claims being generally based upon old concessions granted by natives prior to the taking over of the land by the German Government; and many such claims had never been registered, as the land had always been considered worthless.

In addition to these claimants, several large companies laid claim to the land, others dug up long-forgotten clauses in their charters which gave them a right to "minerals," and in some cases even specified "precious stones should such be found," and in the midst of this confusion new companies were continually being formed. So for a time chaos reigned, during which the licensed prospector was at a great diadvantage, since he never quite knew in pegging a claim whether his title to it would in the end hold good.

And he, as had been the case in Kimberley nearly forty years earlier, gradually disappeared, giving place to various companies, amongst which the better-known, such as Kolmans Kop, and Pomona, had proved, when war broke out in 1914, highly productive. The stones are very small, ranging from one-quarter to an eighth of a carat, but are good quality, and up to August of that year about 5,400,000 carats had been extracted, of an approximate value of nine-and-a-quarter millions sterling. The output was strictly controlled by the German Government, and the sales limited to a little over a million carats annually.

(To be continued)

## THE PHYSICAL CHEMISTRY OF BASIC SLAGS.

By CECIL H. DESCH, D.Sc.,
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Any account of the physical chemistry of basic slags at the present day must of necessity be largely a confession of ignorance. We are still unaware, in spite of much excellent research work on the subject, of the form in which the principal components are combined in the slag. The chemical analyses indicate the proportions in which the metallic and non-metallic oxides occur, and the sulphur percentage is also known, but there is much difference of opinion as to the nature of the silicates and phosphates which compose the slag, and as to the nature of the sulphides which occur in it as minor constituents. Large and very perfectly formed crystals have been isolated in certain instances, but it is not clear that these are identical with the usual constituents of massive slags, or even that they are mineralogically homogeneous substances. As an illustration of this last point, the case of the large and apparently perfectly formed plates sometimes

found in tap cinder from the puddling process may be mentioned. Microscopical examinations of these plates in transverse sections proves them to be intergrowths of fayalite and ferrous oxide or magnetite, resembling the "colonies" of eutectic in white iron, which also have the appearance of definite crystals, but have been shown by Prof. Benedicks to consist of two constituents, closely intergrown.

The essential components of basic slag are the oxides of iron, manganese, calcium, magnesium, silicon, and phosphorus, whilst sulphides of calcium and manganese, and calcium fluoride, may be regarded as accessory components. Only one state of oxidation need usually be considered, but iron may present itself either in the ferric or ferrous form.

As a starting point, the excellent investigation of acid open hearth slag by Messrs. Whiteley and Hallimond may be taken (J. H. Whitely and A. F. Hallimond, *J. Iron and Steel Inst.*, 1919, i., 199). It is shown by these authors that iron occurs chiefly in the form of the orthosilicate, $Fe_2SiO_4$, fayalite, with which the corresponding manganese compound, $Mn_2SiO_4$, tephroite, forms solid solutions. When the proportion of manganese is high, the metasilicate, $MnSiO_3$, rhodonite, is formed, and this may contain some iron in solid solution, but a distinct ferrous metasilicate is not observed. This is confirmed by the present writer's observations of puddling cinders, in which a metasilicate has not been found, even when large proportions of silica are deliberately added. Any such excess appears, both in cinders and in slags, as free silica, usually in the form of tridymite. Excess of iron oxide appears as magnetite, or as solid solutions of similar character, ranging from nearly pure ferrous oxide to crystals richer in ferric iron than magnetite. The growth of such crystals is very characteristic, and they form delicate branched crystallites. In acid slags containing more than 8 per cent of lime, an anorthic metasilicate of calcium, magnesium, iron and manganese is formed, giving to the slag a marked acicular structure. A later paper by the same authors (J. H. Whiteley and A. F. Hallimond, *J. Iron and Steel Inst.*, 1919, ii., 159) shows that eutectics are formed between fayalite and magnetite, and between fayalite and tridymite. The writer has also observed these eutectics, but the further eutectics mentioned by Whiteley and Hallimond, namely, of magnetite and tridymite, and of all three minerals, may perhaps be attributed to imperfect equilibrium. Should they prove to occur in the system in a state of equilibrium, then ferric oxide must be regarded as a separate component.

Leaving aside the question of phosphorus, the basic slags differ from acid slags chiefly in containing a much higher proportion of lime. A glance at the ternary equilibrium diagram for the system lime-magnesia-silica (J. B. Ferguson and H. E. Merwin, *Amer. J. Sci.*, 1919 (iv.), xlviii., 81) will show that a slag containing anything like 40 per cent of lime must be largely made up of the orthosilicate, $Ca_2SiO_4$. The solid solutions of this silicate with the silicates of other metals are very liable to undercooling, with the formation of glass. Consequently, a glassy ground mass is often observed in basic slags, rendering the interpretation of their constition much more difficult. Acid slags are usually very free from glass, and even puddling cinders mostly contain mere traces of it. Sections of basic slag may exhibit glass in which are embedded small crystals of a phosphoric mineral; and it is evident that the constitution of such specimens could only be determined by making experiments in the direction of annealing, and so permitting the crystallisation of minerals from the glass.

Turning now to the phosphorus, it is remarkable that no phosphate of iron, either ferric or ferrous is known which is stable at high temperatures The naturally occurring phosphates are hydrated minerals, and do not yield homogeneous anhydrous products on heating On the other hand the phosphates of calcium are well known Several investigators, however, have shown that silicophosphates are the principal constituents of phosphoric basic slags. The first of these compounds was described by Carnot, who attributed to it the formula $Ca_3(PO_4)_2$, $Ca_2SiO_4$ (A. Carnot Richard and Daubre, *Compt. Rend.*, 1883, xcvii. 136). In 1887, Stead and Ridsdale described crystals of a compound also containing phosphate and silicate, $4Ca_3(PO_4)_2$, $Ca_3SiO_5$ (J. E. Stead and C. H. Ridsdale, *Trans. Chem. Soc.*, 1887, li., 601) Other similar compounds have been described and their composition is reviewed by Kroll (V. A Kroll, *J. Iron and Steel Inst.*, 1911, ii., 126), who added yet another, Thomasite, to which he attributed the composition $Ca_3(PO_4)_2$, $3CaO$, $Ca_2SiO_4$ At an earlier period, Hilgenstock (G. Hilgenstock *Stahl u. Eisen*, 1883) had described a tetrabasic phosphate, $4CaO$, $P_2O_5$, and this was long regarded as the essential constituent of all slags which were of agricultural value. It is more likely that the silicophosphates are the valuable compounds. As a rule, these compounds have been described by their external characters only and very little is known as to their mineralogical individuality. It must be remembered that calcium is replaceable to a greater or less extent in such compounds by iron and other metals, and it is quite possible to find slags, the analysis of which will permit of inclusion under the formula of Thomasite given above. It does not follow that these slags are pure individuals; they may be eutectic intergrowths simulating pure crystals as mentioned above. When phosphorus is added in moderate quantities to puddling cinders, no new constituent makes its appearance, and phosphorus compounds can evidently pass into solid solution in siliceous iron minerals. The examination of specimens polished on one surface only and etched, as in the examination of metallographic specimens, usually gives much more information than the study of thin sections, although the application of polarised light to the latter affords a useful means of idenifying minerals by their optical properties when their limits have been once defined. The fine eutectics in slags and cinders are generally overlooked in thin sections

Sulphides enter into solutions to an unknown extent, but a part may remain in insoluble globules. Fluorides combine with phosphates to form minerals of the apatite class, and this, no doubt, accounts for the insolubility, under agricultural conditions, of slags containing fluorspar Beyond this, little can be stated definitely as to the constitution of the basic slags without further research, the performance of which is highly desirable.—*Transactions of the Faraday Society* December, 1920.

# THE USE OF GALLIUM FERROCYANIDE IN ANALYSIS.

By LYMAN E. PORTER and PHILIP E. BROWING.

It has been shown that gallium may be separated from many elements by precipitation as the ferrocyanide from a solution containing as much as a third of its volume of concentrated hydrochloric acid (Lecocq de Boisbaudran, *Compt. Rend.*, 1882-1883, xciv., 1154, 1228, 1439, 1628; xcv., 157, 410, 503, 1192; 1332; xcvi., 152, 1696, 1838; xcvii., 142, 295, 522, 623, 730, 1463; Browning and Porter, *Am. J. Sci.*, 1917, xliv., 221). Two problems arise in connection with the application of this reaction in analytical work, namely, filtration and the recovery of the gallium from the precipitated salt free from iron and the ferrocyanide radical. This paper gives the results of a study of these points.

The precipitate of gallium ferrocyanide is very gelatinous and, while it is possible to filter it on an ordinary paper filter, the filtration is very slow and it is difficult to wash the material. The large bulk of the precipitate and the slowness with which it settles make it impossible to decant the liquid with any success. The effect of changing the acid concentration and of precipitating the material in the presence of electrolytes such as potassium chloride and ammonium chloride was studied, but it was found that the precipitate does not settle any better under these conditions. Adding the reagent to the hot solution likewise failed to make any appreciable difference in the form of the precipitate and in its speed of filtration.

Various modifications of paper and asbestos filters were tested in an attempt to hasten the filtration. The use of asbestos or of paper on a Gooch crucible was found impossible, the precipitate passing through even a thick layer of the material, as it does likewise through paper on a funnel when suction is applied. If, however, a mat of fine filter paper fibre, best made by scratching some paper with a knife, is washed into the funnel, containing a double filter paper, the gallium ferrocyanide is held on it, provided the suction is not applied too strongly. If, as is often the case, the first portion of the filtrate is cloudy, it should be poured through the filter again, the resulting filtrate being clear. This process can be carried out in much less time than is required for the filtration of the same amount of material without the use of suction. Of two solutions, containing equal amounts of the gallium precipitate in 10 cc. of liquid, one required 15 minutes to be filtered once through a paper filter without suction, whereas the second, by the use of the method just described, was completely filtered in two minutes, including the second filtration of part of the solution. Table I. shows the results of the quantitative determination of gallium as the ferrocyanide, the filtration having been made with suction. The material was ignited and weighed as the mixed oxides of gallium and iron (*Compt. Rend.*, 1882, xciv., 1228), in the gallium ferrocyanide salt, $Ga_4(FeC_6N_6)_3$. If some of the iron remains as the carbide, as is probably the case, the resulting weight is not affected, on account of the identity of the molecular weights of $Fe_2O_3$ and $2FeC_2$ (Treadwell-Hall. "Analytical Chemistry," 4th ed., i., 320).

TABLE I.

| | Gallium oxide taken. G. | Mixed oxides calculated. G. | Mixed oxides found G. | Error G. |
|---|---|---|---|---|
| 1. | 0·0236 | 0·0386 | 0·0400 | 0·0014 |
| 2. | 0·0236 | 0·0386 | 0·0395 | 0·0009 |

This method of direct ignition is not specially recommended, as it gives high results which in small amounts of material show high percentage errors. It was, however, thought best to include it in the general study of the problem.

The recovery of gallium from the ferrocyanide by the ignition with ammonium nitrate and the subsequent separation of the gallium from iron by means of sodium hydroxide has been described by us (Browning and Porter, *loc. cit.*). The possibility of recovering the gallium without the formation of ferric or ferrous salts and the necessity of separating it from these was studied. When the precipitated gallium ferrocyanide is treated with an alkali in solution it is decomposed into the soluble alkali salts of gallium and of ferrocyanide. It was found that when carbon dioxide is bubbled through such a solution to saturation the gallium is quantitatively precipitated as hydroxide, or basic carbonate, in a form easy to filter and readily washed free from ferrocyanide. This behaviour is analogous to the reaction utilised in the detection of the constituents of zinc ferrocyanide (Treadwell-Hall, "Analytical Chemistry," 4th ed., i, 319). Table II. shows some results on the quantitative estimation of gallium after its precipitation as the ferrocyanide and the recovery of the gallium as described above. The ferrocyanide precipitate was in each case filtered on paper after standing for two days. In Expt. 1 the paper with the precipitate was treated directly in a beaker with sodium hydroxide solution and carbon dioxide, the precipitate and paper being filtered off. In Expt. 2. the precipitate was filtered and dissolved off the paper by sodium hydroxide solution and then treated with the carbon dioxide. In the other cases the ferrocyanide was filtered on paper with suction in the presence of paper fibre, dissolved in sodium hydroxide solution and finally precipitated by carbon dioxide from a volume of 100 cc.

TABLE II.

| | $Ga_2O_3$ taken. G. | $Ga_2O_3$ found G. | Error G. |
|---|---|---|---|
| 1. ... ... ... | 0·0472 | 0·0466 | —0·0006 |
| 2. ... ... ... | 0·0236 | 0·0215 | —0·0021 |
| 3. .. ... ... | 0·0236 | 0·0225 | —0·0011 |
| 4. ... .. ... | 0·0236 | 0·0238 | +0·0002 |
| 5. ... ... .. | 0·0944 | 0·0951 | +0·0007 |
| 6. .. ... ... | 0·1038 | 0·1035 | —0·0003 |

When an alkaline solution of gallium ferrocyanide is boiled with ammonium chloride a precipitate of gallium is formed, which consists chiefly of the ferrocyanide. If, however, the ferrocyanide is oxidised over to the ferricyanide by hydrogen peroxide in alkaline solution before the ammonium chloride treatment, the precipitate obtained is gallium hydroxide free from any cyanide radicals, as shown by qualitative tests. The oxidation may be made with a nitrate, but the peroxide method is the more satisfactory. This method for the recovery of gallium from the ferrocyanide works well and is rather quicker than the carbon dioxide method. Quantitative results are given in Table III. of some determina-

ons by this method in which the gallium was pre- pitated as the ferrocyanide and dissolved rectly in sodium hydroxide without previous ltration.

TABLE III.

| | $Ga_2O_3$ taken. G. | $Ga_2O_3$ found. G. | Error G. |
|---|---|---|---|
| ... ... ... | 0·0956 | 0·0952 | —0·0004 |
| ... ... ... | 0·1044 | 0·1033 | —0·0011 |

Of the elements commonly associated with gal- um, whose salts are soluble in alkali, zinc is the ost common one that forms an insoluble ferro- anide. The insolubility of zinc ferricyanide in id and in ammonium hydroxide makes the paration of gallium from the ferrocyanide by eans of the peroxide method impossible if zinc present. In such a case, however, either of the llowing two methods may be employed.

In the first case the mixed ferrocyanides are dis- lved in sodium hydroxide solution and the bases ecipitated together by carbon dioxide. The gal- um may now be separated from the zinc by dis- lving the precipitate in hydrochloric acid and iling the solution with ammonium acid sulphite precipitate the gallium (Porter and Browning, *ur. Amer Chem. Soc.,* 1919, xli., 1491). The llowing procedure may also be used. The alkali lution of the ferrocyanides is treated with hydro- en sulphide to precipitate the zinc (Browning d Porter, *loc. cit.*), which even in the presence the ferrocyanide is precipitated as the sulphide. rom the filtrate the gallium may be recovered ee from ferrocyanide either by precipitation with rbon dioxide, or by boiling with ammonium loride after the oxidation of the excess of sul- ide and of the ferrocyanide by hydrogen per- xide.

*Summary.*

1. A method of filtering gallium ferrocyanide ith suction has been described.
2. Methods for the recovery of gallium from s ferrocyanide salt by alkali and carbon dioxide y sodium hydroxide, and by hydrogen peroxide d ammonium chloride have been developed.
3. Methods for the recovery of gallium from s ferrocyanide in the presence of zinc have been escribed.—*Journal of the American Chemical ociety,* January, 1921.

## THE FARADAY SOCIETY.

ENERAL DISCUSSION ON "THE FAILURE OF METALS UNDER INTERNAL OR PROLONGED STRESS."

HE General Discussion on this subject which is eing organised jointly by the Faraday Society, stitution of Mechanical Engineers, Institute of etals, and the Iron and Steel Institute will take lace on Wednesday, April 6 next There will be oth afternoon and evening sessions. The North- ast Coast Institution of Engineers and Ship- uilders, The Institution of Engineers and Ship- uilders in Scotland, and the West of Scotland ron and Steel Institute are also participating in e Discussion.

A preliminary programme has been issued which ates that the Discussion will be opened by Dr. V. Rosenhain, F.R.S., who will give a general survey of the subject. Among other contributions on specific aspects of the subject which are ex- pected are :—

"Chemical Influences in the Failure of Metals under Stress." By Prof. C H. Desch.

"Mechanism of Failure in Metals from Internal Stress." By Dr. W. H. Hatfield.

"The Removal of Internal Stress in Brass." By H. Moore and S. Beckinsdale

"The Season-Cracking of Brass : Digest of Pub- lished Information" By Harold Moore.

"Notes on Fractures in Certain Steel Tubes." By Sir Henry Fowler.

"Intercrystalline Cracking of Mild Steel." By J. A. Jones.

"The Presence of Internal Fractures in Steel Rails and their Relations to the Behaviour of the Material under Service Stresses." By H. S. Rawdon.

"The Spontaneous Cracking of Necks of Small Arm Cartridge Cases." By W. C. Hothersall.

"The Internal Stresses in Brass Tubes." By R. H. N. Vaudrey and W. E. Ballard.

"The Failure of Condenser Tubes."By Commdr. W. Campbell, U.S.N.R.F.

"Note on Corrosion and Season-Cracking." By G. D. Bengough.

"Corrosion Cracking of Non-Ferrous Materials." By W. R. Woodward.

"Stress and Season-Cracking in Cold-Worked Brass Articles." By Dr. F. Rogers.

"Effects of Prolonged Stress on Metals at High Temperatures." By Dr. F. Rogers.

"Internal Stresses in Relation to Microstructure." By J. C. Humfrey.

"Failure of the Lead Sheathing of Telegraph Cables." By L. Archbutt.

Other contributions will probably be made by Prof. C. Benedicks, Mr. W. O. Ellis, Dr. F. C A. H. Lantsberry, Dr A. McCance, Dr. E. A. Smith, Prof. T. Turner, Mr. J. E. Howard, Dr. F. C. Thompson, Prof. C. H. Matthewson, Dr. R. S. Hutton, Mr. B. S. Haigh, Mr. R. W. Webster.

An exhibition of specimens will be held in con- nection with the meeting, and those desirous of lending specimens are asked to communicate with Mr. F. S. Spiers, Secretary to the Joint Com- mittee, 10, Essex Street, Strand, W.C.2.

THE ACTION OF WATER ON WOOL.—When a small sealed tube, containing woollen threads in water is heated to a temperature of 130°-135° C., the wool undergoes a decrease in volume. The shrinkage, easily noted, corresponds with a pro- found change in the structure of the wool. The fibres placed between crossed Nicol prisms no longer display the characteristic birefrigency of the primitive wool, and they are also pulverisable dry. The wool can be attacked by water under pressure or by steam; in fact, in the autoclave the same results are observed, but more slowly than with liquid water. With HCl instead of water, results are analogous. Working with a diluted solution of potash (1/20 N for example) the wool shrinks at a lower temperature and at 130° C, disaggregation commences and finally the fibres are completely dissolved.—*Bull. Soc. Chim. de France,* January 20, 1921.

## PROCEEDINGS OF SOCIETIES.

### PHYSICAL SOCIETY.

*Annual General Meeting, February 11, 1921.*

PROF. SIR W. H. BRAGG, F.R.S., President, in the Chair.

THE report of the Council was read by the Secretary, Mr. F. E. Smith. The report was unanimously adopted. The report of the Treasurer was read by Mr. W. R. Cooper. The report was unanimously adopted. Votes of thanks to the Honorary Auditors, the Officers and Council, and the Governing Body of the Imperial College were unanimously passed, the respective proposers and seconders being Dr. Chree and Dr. Lister, Mr. Clark and Dr. Borns, Dr. Thomas and Mr. Paul.

The scrutators, after examination of the ballot papers, declared the Officers and Council for the ensuing year to be elected in accordance with the following list:—

*President*—Prof. Sir W. H. Bragg, C.B.E., M.A., F.R.S. *Vice-Presidents* (who have filled the office of President)—C. Chree, Sc.D., LL.D., F.R.S.; Prof. H. L. Callendar, M.A., LL.D., F.R.S.; Prof. R. B. Clifton, M.A., F.R.S.; Sir Richard Glazebrook, K.C.B., D.Sc., F.R.S.; Sir Oliver J. Lodge, D.Sc., F.R.S.; Prof. C. H. Lees, D.Sc., F.R.S.; Prof. A. W. Reinold, M.A., F.R.S.; Sir Arthur Schuster, Ph.D., Sc.D., F.R.S.; Sir J. J. Thomson, O.M., D.Sc., F.R.S.; Prof. C. Vernon Boys, F.R.S. *Vice-Presidents*—Prof. W. Eccles, D.Sc.; Prof. A. S. Eddington, M.A., M.Sc., F.R.S.; The Rt. Hon. Lord Rayleigh, F.R.S.; Prof. Sir Ernest Rutherford, D.Sc., F.R.S. *Secretaries*—F. E. Smith, O.B.E., F.R.S., National Physical Laboratory, Teddington; D. Owen, B.A., D.Sc., 62, Wellington Road, Bush Hill Park, N. *Foreign Secretary*—Sir Arthur Schuster, Ph.D., Sc.D., F.R.S. *Treasurer*—W. R. Cooper, M.A., B.Sc., 82, Victoria Street, S.W.1. *Librarian*—Prof. A. O. Rankine, D.Sc., Imperial College of Science and Technology. *Other Members of Council*—G. B. Bryan, D.Sc.; C. R. Darling, F.I.C.; Prof. C. L. Fortescue, O.B.E.; E. Griffiths, D.Sc.; F. L. Hopwood, D.Sc.; E. H. Rayner, M.A., D.Sc.; A. Russell, M.A., D.Sc.; T. Smith, B.A.; J. H. Vincent, D.Sc., M.A.; Prof. W. B. Morton, M.A.

After the conclusion of the general business, a discussion on "*Absolute Measurements of Electrical Resistance, and Instruments based on the Temperature-Variation of Resistance*" was held.

SIR RICHARD GLAZEBROOK opened the discussion with a historical review of the work of early workers on absolute resistance measurements and the gradually increasing accuracy which had been obtained in such measurements with the development of improved methods and apparatus.

Mr. F. E. SMITH wished to confine himself to two suggestions. The first was that the accuracy of absolute determinations being now in excess of the accuracy with which the International Mercury Standard could be reproduced, such a standard was now useless, and workers should express their results in true ohms rather than in international ohms. His second suggestion was that teachers should familiarise their students with absolute methods of resistance measurement, and he showed a simple apparatus with which such measurements could be made in the laboratory in a few minutes.

Prof. H. L. CALLENDAR explained the principles of his temperature-compensated resistance bridge, and exhibited various resistance thermometers for special purposes and several instruments for radiation measurements.

Mr. C. R. DARLING described the early work of Siemens on resistance thermometry.

Major TUCKER exhibited and described his hot-wire microphone.

Prof. J. T. MCGREGOR MORRIS exhibited and described a robust and portable hot-wire anemometer.

Miss HARGOOD-ASH, in the absence of Prof. Leonard Hill, exhibited and explained the latter's "Calcometer."

Mr. E. A. GRIFFITHS exhibited and described a resistance gauge for measuring the depth of liquid in a tank.

Mr. A. H. DAVIS read a Paper on "*An Instrument for Measuring Convected Heat.*"

Dr. J. S. G. THOMAS exhibited and explained his Directional Hot-wire Anemometer.

Dr. DAYNES, in the absence of Dr. G. A. Shakspear, exhibited and explained the latter's gas permeameter.

Other instruments were exhibited, but owing to the lateness of the hour were not described.

## PAPERS RECEIVED.

"Polymerisation amongst Liquids." By W. R. FIELDING, M.A., M.Sc. (Vict.).

A continuation of "Polymerisation in the Solid State" (CHEMICAL NEWS, cxxii., No. 3170). After finding the value of $p$ for different elements and compounds, the author makes special reference to water and typical organic compounds, which yield striking results. February 21, 1921.

## BOOKS RECEIVED.

"The Extra Pharmacopœia." Vol. I. 17th Edition. By W. H. MARTINDALE, Ph.D., Ph.Ch., F.C.S., and W. W. WESTCOTT, M.B., D.P.H. 1115 pages. Price 27s. net. London: H. K. Lewis & Co.

"Treatise on General and Industrial Chemistry." By Dr. ETTORE MOLINARI. Second Edition, edited by THOMAS H. POPE, B.Sc., F.I.C., A.C.G.I. With 382 illustrations and two Plates. Price £2 2s. London: J. & A. Churchill.

"A Text-book of Inorganic Chemistry for University Students." By J. R. PARTINGTON, M.B.E., D.Sc. Price 25s. net London: Macmillan & Co.

"Introduction to Qualitative Chemical Analysis." By TH. WILHEIM FRESENIUS. 17th edition of the original work, by C. REMIGIUS FRESENIUS, Translated by C. AINSWORTH MITCHELL, M.A. (Oxon.), F.I.C., Editor of the *Analyst*. With 57 Illustrations, xix+954 pages. Price 36s. net. London: J. & A. Churchill.

"A Text-book of Inorganic Chemistry." By J. NEWTON FRIEND, Ph.D., F.I.C. Vol. IX., Part I. Cobalt, Nickel, and the Elements of the Platinum Group. xvii. + 367 Pages. London: Charles Griffin, Ltd.

## NOTES.

BRITISH ENGINEERING STANDARDS ASSOCIATION.—A British Standard Specification has been issued by the British Engineering Standards Association for benzol for motor fuel, commonly known as "benzole," a benzene mixture. The specification includes a definition of the term "benzole", a description of the substances and notes on its physical and chemical properties. This is followed by appendices giving necessary tests, including that for the estimation of the sulphur content, with diagram, and the specification concludes with a description and illustration of the standard distillation apparatus. This subject has engaged the activities of the Association for some months past, and the Committee, under the chairmanship of Dr. G. Rudorf, has had the co-operation of the following Government Departments and industrial and scientific organisations: War Office, Air Ministry, H.M. Petroleum Department, National Physical Laboratory, Institution of Automobile Engineers, Institution of Chemistry of Great Britain and Ireland, Association of British Chemical Manufacturers, Auto-Cycle Union, Automobile Association and Motor Union, British Chemical Trade Association, Commercial Motor Users' Association, National Benzole Association, Oil and Colour Chemists' Association, Society of British Aircraft Constructors, Society of Chemical Industry. The specification can be obtained from the Secretary of the British Engineering Standards Association, 28, Victoria Street, London, S.W.1., price 1s. 2d., post free.

## NOTES AND QUERIES.

ENQUIRY.—Will some correspondent be good enough to recommend some book dealing with the latest practice in preparing steel samples for micro-examination, more particularly the best reagents and methods for differentiating between the various constituents, such as sulphur, phosphorous, slag, silico-sulphide, etc.—STUDENT.

## New Patents.

THIS List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W.C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

4895—Armour Fertilizer Works.—Production of aluminium chloride. Feb. 11th.
4556—Attack, F. W.—Condensation of o-benzoyl-benzoic acid or its derivatives. Feb. 9th.
4557—Attack, F W.—Oxidation of hydrocarbons. Feb. 9th.
4637—Bader, W.—Manufacture of anhydride, etc. Feb. 9th.
4637—British Cellulose & Chemical Manufacturing Co., Ltd—Manufacture of acetic anhydrides, etc. Feb 9th.
4642—Cumberland Coal Power & Chemicals Ltd.—Production of hydrogen. Feb. 9th.

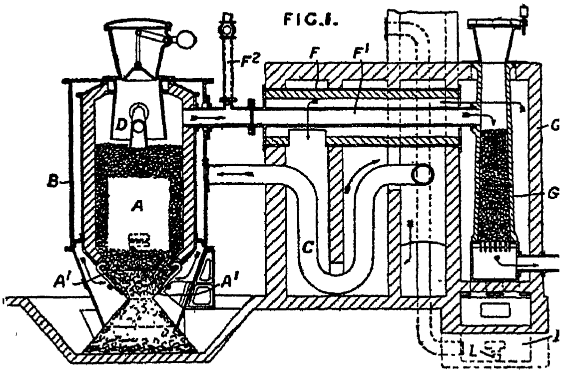
*Specification published this Week.*

128895—Soc Industrielle de Products Chimiques.—Separation o the double salt sodium ammonium sulphate into sodiun sulphate and ammonium sulphate.
158288—MacLeod, J. G.—Processes for the production of hydroger sulphide from sulphurous gases
154170—Terrisse, H. and Levy M.—Process of and apparatus fo regenerating hydrochloric acid used in the manufacture o glucose.

*Abstract Published this Week.*

*Ammonia.*—Mr. A. Rollason of Long Eaton, Derbyshire, has beer granted a Patent No. 155313 for apparatus for producing Ammoni in which a mixture of air and steam is preheated in a pipe C and jacket B of a producer A, and is then passed through gates $A^1$ int the fuel, the level of which is kept constant by a bell D. Th temperature in the producer is maintained below 950° C, and the a is wholly deprived of oxygen. The exit gas is cooled to 500° C by cooler or by steam admitted from a pipe $F^2$, and is then passe through a tube $F^1$ surrounded by an outer tube F and is there heate to 550-600° C, by which means it is stated that the molecules o nitrogen are dissociated into atoms. The gas passes from the pip $F^1$ through a column G of coke mixed with 5% of limeston maintained by external heating at 700-800° C. Ammonia is produce and is recovered after cooling to 90° C The remaining gas i introduced into the combustion chamber at L and burnt, th products passing through the casing I to the space between th walls G and $G^1$ and thence as shown by the arrows.

FIG. I.




Messrs. Rayner & Co., will obtain printed copies of th published specifications and will forward on post free for the officia price of 1/- each.

## MEETINGS FOR THE WEEK

*Monday, March 7.*

Royal Institution, 5. (General Meeting).
Royal Society of Arts, 8. "X-Rays and their Industrial Applica tions" by Major G. W C. Kaye.
Society of Chemical Industry, 8
Institution of Electrical Engineers, 7. (At Cardiff).

*Tuesday, March 8.*

Royal Institution, 3. "Darwin's Theory of Man's Origin" by Prof Arthur Keith.
Society of Chemical Industry. (At Edinburgh).
Institution of Electrical Engineers, 7. (At Leeds, Manchester an Edinburgh).
Institute of Metals, 8. (At Glasgow).

*Wednesday, March 9.*

Royal Society of Arts, 8.
Institute of Metals, 10.30 and 2.30. (Annual Meeting).

*Thursday, March 10.*

Royal Institution, 3. "The Meteorology of the Antarctic" b Dr. G. C. Simpson.
Society of Chemical Industry. (At Birmingham).
Institute of Chemistry. (At Liverpool).
Institute of Metals, 10.30 and 2.30 (Annual Meeting).
Institution of Electrical Engineers, 6.
Optical Society, 7.30.

*Friday, March 11.*

Royal Institution, 9. "Medical Idiosyncrasies" by Dr. J. Freemar
Physical Society, 5.
Institution of Electrical Engineers, 6.30.

*Saturday, March 12.*

Royal Institution, 3. "Electricity and Matter" by Sir Ernes Rutherford.

## NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemical Apparatus, &c., for review or notice to be addressed to the EDITOR.

**SUBSCRIPTIONS**, £1 12s. per annum, payable in advance, should be addressed to the MANAGER.

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PATENTS, TRADE MARKS. Handbook and advice free—B. T. KING, British and U. S. Regd. Patent Attorney, 146a, Queen Victoria St., London. 35 years reference

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FOR SALE—*Journal of the Chemical Society*, from 1885 to date. New. Offers, X., CHEMICAL NEWS 97, Shoe Lane, E.C.4.

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THE CHEMICAL NEWS.

VOL. CXXII, No. 3178.

## THE COMPOSITION OF DOLOMITES.

By IRENE EVERMAN, O'NEAL MASON and GLENN BROWNING.

THE work on dolomites that has been carried on in the chemical department of Cornell College is still in progress, and the results of some recent analyses are recorded in this paper. We are obtaining specimens from as many different localities as possible, in order to examine the physical as well as the chemical characteristics.

1. Specimen from Le Grand, Iowa.—It is of a buff colour, compact, and somewhat crystalline, with transparent rhombohedral crystals disseminated throughout the specimen.

| | Per cent. |
|---|---|
| $SiO_2$ | 1·17 |
| $Al_2O_3$ | 0·31 |
| $Fe_2O_3$ | 8·75 |
| $MgCO_3$ | 11·65 |
| $CaCO_3$ | 78·33 |
| Total | 100·21 |

The specific gravity is 2·64.

The analysis shows a magnesian limestone, rather than a true dolomite.

2. Specimen from near Gouverneur, New York.—It is a mixture of grey and white crystals, resembling ordinary marble.

| | Per cent. |
|---|---|
| $SiO_2$ | 0·39 |
| $Al_2O_3$ | 2·72 |
| $Fe_2O_3$ | 0·17 |
| $CaCO_3$ | 67·24 |
| $MgCO_3$ | 29·88 |
| Total | 100·40 |

The specific gravity is 2·94.

The rock approaches a dolomite in composition, but the calcium carbonate too largely predominates for a typical specimen.

3. Specimen from Cape Breton Island. It was kindly sent by the Hon. D. Ross MacDonald, to whom we express our thanks.

| | Per cent. |
|---|---|
| $SiO_2$ | 5·19 |
| $Al_2O_3$ | 2·54 |
| $Fe_2O_3$ | 0·41 |
| $CaCO_3$ | 53·12 |
| $MgCO_3$ | 38·49 |
| Total | 99·75 |

The specific gravity is 2·83.

The rock approaches a true dolomite in composition.

4. Specimen from Frizington, Cumberland, England.—These are rhombohedral crystals on fluorite, coloured light brown by the presence of iron. The specific gravity was not determined.

| | Per cent. |
|---|---|
| $SiO_2$ | 0·47 |
| $Al_2O_3$ | 1·10 |
| $Fe_2O_3$ | 21·27 |
| $MgCO_3$ | 25·91 |
| $CaCO_3$ | 51·05 |
| Total | 99·80 |

The specimen contains a large amount of iron, which replaces a portion of the magnesium, but in other respects it resembles a true dolomite.

5. Specimen from the Marquette District, Michigan. The dolomite as crystals is deposited on a slate-coloured background The botryoidal structure is composed of rhombohedral crystals having a specific gravity of 2 75.

| | Per cent |
|---|---|
| $SiO_2$ | 0·28 |
| $Al_2O_3$ | 4·16 |
| $Fe_2O_3$ | 0·66 |
| $CaCO_3$ | 49·83 |
| $MgCO_3$ | 45·48 |
| Total | 100·41 |

The specimen contains a relatively large amount of magnesium carbonate, and is quite a typical dolomite.

6. Specimen from Tuchshoe, New York.—Traces of iron colour the otherwise white crystals. They are rhombohedral in form, hard, and possess a bright lustre. The specific gravity is 2·84.

| | Per cent. |
|---|---|
| $SiO_2$ | 0·45 |
| $Al_2O_3$ | 0·16 |
| $Fe_2O_3$ | 0·10 |
| $MgCO_3$ | 46·80 |
| $CaCO_3$ | 52·16 |
| Total | 99·76 |

The specimen is quite a typical dolomite.

7. Specimen from New Almadin, California — The crystals are white on a grey background. The rhombohedrals are collected in scale-like masses, and are quite brilliant in lustre. The specific gravity is 2·88.

| | Per cent. |
|---|---|
| $SiO_2$ | 0·29 |
| $Al_2O_3$ | 0·00 |
| $Fe_2O_3$ | 5·57 |
| $CaCO_3$ | 53·41 |
| $MgCO_3$ | 40·96 |
| Total | 99·45 |

8. Specimen from Providence, Rhode Island.—The rather soft rhombohedral crustals containing traces of visible iron oxide rest on a crystalline base. We could not secure a sufficiently large mass to obtain the specific gravity.

| | Per cent. |
|---|---|
| $SiO_2$ | 0·75 |
| $Al_2O_3$ | 0·00 |
| $Fe_2O_3$ | 2·19 |
| $CaCO_3$ | 61·50 |
| $MgCO_3$ | 35·63 |
| Total | 100·07 |

The specimen approaches a true dolomite in composition.

9. Specimen from White Pine, Nevada.—The rhombohedral crystals are white on a brown and grey surface, and are rather soft. The crystals on analysis were found to contain a small amount of copper. We were not able to determine the specific gravity.

| | Per cent. |
|---|---|
| $SiO_2$ | 2·16 |
| $Al_2O_3$ | 24·24 |
| $Fe_2O_3$ | 0·00 |
| $CaCO_3$ | 72·83 |
| $MgCO_3$ | 0·31 |
| Cu | 0·86 |
| Total | 100·40 |

The specimen is in no sense a dolomite, but a limestone containing only a small amount of magnesium.

10. Specimen from Guanajuato, Mexico.—The specimen is white, with visible traces of iron oxide. The crystals are hard, and hexagonal in form. We were not able to determine the specific gravity.

| | Per cent. |
|---|---|
| $SiO_2$ | 86·76 |
| $Al_2O_3$ | 4·33 |
| $Fe_2O_3$ | 5·50 |
| $MgCO_3$ | 2·11 |
| $CaCO_3$ | 0·75 |
| Total | 99·45 |

The specimen is not a dolomite, but quite an ordinary sandstone.

11. Specimen from Nagyrag, Trannsylvania.—Rhombohedral crystals on quartz.

| | Per cent. |
|---|---|
| $SiO_2$ | 46·33 |
| $Al_2O_3$ | 43·28 |
| $Fe_2O_3$ | 1·83 |
| $CaCO_3$ | 2·93 |
| $MgCO_3$ | 5·05 |
| Total | 99·41 |

The analysis doubtless shows a clay and not a dolomite.

12. Specimen from Clayton, Iowa.—This takes a good polish, when it resembles brown marble. It belongs to the Plattville formation of the Ordovician in the Lower Silurian.

| | Per cent. |
|---|---|
| $SiO_2$ | 0·87 |
| $Fe_2O_3$ and $Al_2O_3$ | 1·01 |
| $CaCO_3$ | 53·34 |
| $MgCO_3$ | 44·44 |
| Total | 99·66 |

The specific gravity is 2·69. The analysis shows the specimen to be a typical dolomite.

13. Specimen from Dubuque, Iowa.—It is of a grey colour, and quite compact in texture. It belongs to the same geological formation as the preceding.

| | Per cent. |
|---|---|
| $SiO_2$ | 7·29 |
| $Fe_2O_3$ and $Al_2O_3$ | 3·00 |
| $CaCO_3$ | 46·94 |
| $MgCO_3$ | 42·89 |
| Total | 100·12 |

The specific gravity is 2·83. It is quite a typical dolomite.

Cornell College, Chemical Department.
January, 29, 1921.

## THE DETERMINATION OF THE CARBON DIOXIDE IN COAL.*

By F. S. SINNATT, M.B.E., M.Sc. (Tech.), F.I.C., M.I.Min.E.
(Director of Research to the Association) and
W. HARRISON, F.C.S.

*Literature.*

A close examination of the literature shows that few results have been published of determinations of the amount of carbon dioxide evolved when coal is treated with acids. One reason for this probably lies in the fact that the ordinary methods for the estimation of carbon dioxide in carbonates are not easy to apply to coal. The amount of carbonates varies within wide limits in different seams, but as a rule is comparatively small.

The information is important for two main reasons: (1) It is not possible to ascertain the percentage of carbon in coal unless that occurring as carbonates, etc. is known. The value obtained in the ordinary method of determining carbon by combustion includes the carbon occurring both in the organic substance and in the carbonates, etc. If the exact percentage of organic carbon in the coal is required, that occurring in the carbonates must be determined, and deducted from the total carbon found by combustion. Certain coals contain up to 5 per cent of substituted calcium carbonates, which is equivalent to approximately 0·5 per cent of carbon. It follows that the percentage of organic carbon in the coal is 0·5 per cent lower than that found by the combustion. This is of some importance when considering the calorific value of coal, as 0·5 per cent of carbon is equivalent to 41·6 calories, or 74·8 B.T.U.'s per pound. In certain abnormal specimens of coal 30 per cent calcium carbonate have been found.

(2) A knowledge of the amount of carbon dioxide occurring as carbonates is also an auxiliary means of obtaining an idea of the composition of the inorganic compounds present in coal. In a later paper, a number of anlyses will be given of the white partings (ankerites) occurring in Lancashire seams. These compounds are fairly constant in composition in a particular seam; if the composition of the ankerites is found by analysis, including the percentage of carbon dioxide present, it is possible to calculate approximately the composition of the particular compound contained in a sample of coal by a simple determination of the carbon dioxide.

The following processes for the determination of carbon dioxide in carbonates are in general use:—

Schroetter's apparatus, and various modifications may be expected to yield results within 1 per cent, when the percentage of carbon dioxide in the compound is high, and at least 1 grm. is available. The method has been found to be useless for the determination of carbon dioxide in coal.

S. H. Collins (*J.S.C.I.*, 1906, xxv., 519) describes an improved form of Scheibler's apparatus, in which the carbon dioxide evolved from carbonates by the action of acids is collected and measured. The method suffers from the inaccuracies inherent in any process where the measurement of small volumes of carbon dioxide are necessary. The equivalence of six sources of error is stated to be 1 per cent.

* Read before the Lancashire & Cheshire Coal Research Association

A method for the determination of small percentages of carbonates in such material as soil is described by Hall & Russell (*J. Chem. Soc.*, 1902, lxxxi., 83), who state that where the amount of calcium dioxide present is only about 0·5 per cent, the whole of the carbon dioxide produced when acid is added may remain dissolved in the reaction products

The method most generally used is to decompose the carbonates with a suitable acid, and after purifying the carbon dioxide produced, to aspirate it through weighed potash bulbs. Unless the weight of carbon dioxide produced is considerable, the process is quite inaccurate, even when the precaution of counterpoising the potash is adopted; considerable variations in weight of the potash bulbs are possible from external sources.

A number of methods in which standard barium hydrate solution is used for the absorption of carbon dioxide have been described. The general procedure advocated is to place the standard solution in some type of wash bottle, but the process has not been generally adopted, largely for the following reasons:—

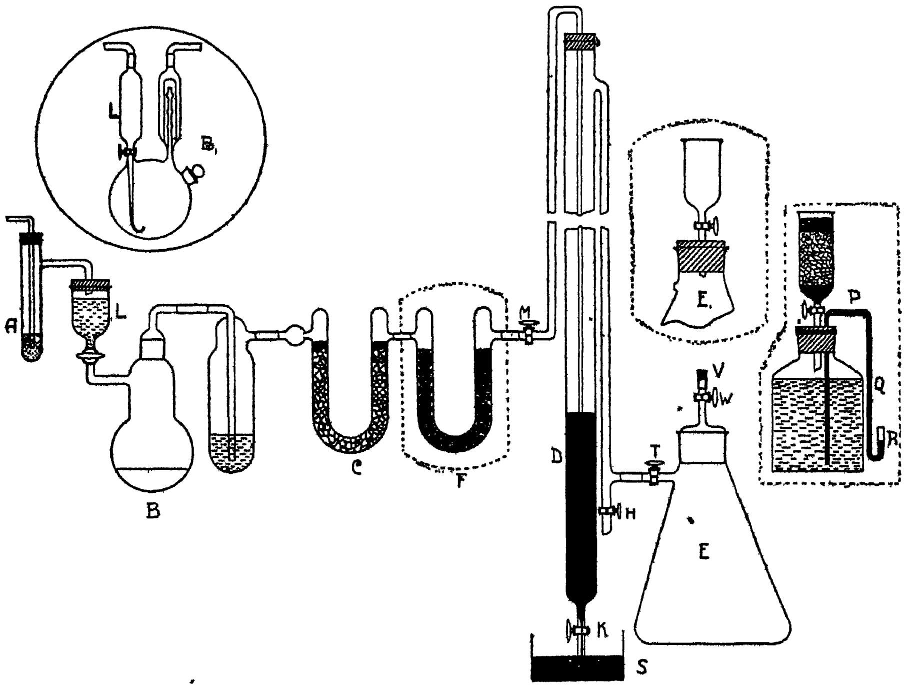
Barium hydrate is only comparatively slightly soluble in water, which necessitates the use of a large volume of solution, and consequently a cumbersome wash bottle; the rate of absorption of carbon dioxide by barium hydrate solution is comparatively low, and consequently a slow stream of gas is essential in order to effect complete absorption. It is difficult, without introducing considerable elaboration to prevent the barium hydrate solution coming into contact with the air, or the breath of the experimenter during the manipulation of the process.

One of us (*Analyst*, 1912, xxxvii., 12) described an apparatus by means of which the rate of flow of a gas into an evacuated vessel could be controlled, and later (*Analyst*, April, 1913) showed that the apparatus could be adopted for the accurate determination of carbon dioxide in carbonates. From the latter paper the following estimations may be quoted, as indicating the degree of accuracy attained by the method:—

| Weight of calcite. Grms. | | Carbon dioxide found. Grms. | | Carbon dioxide calculated. Grms. |
|---|---|---|---|---|
| 0·1310 | ... | 0·0576 | ... | 0·0575 |
| 0·1710 | ... | 0·0754 | ... | 0·0751 |
| 0·0826 | ... | 0·0364 | ... | 0·0363 |
| 0·3490 | ... | 0·1526 | ... | 0·1534 |
| 0·0785 | ... | 0·0341 | . | 0·0345 |

*Apparatus.*

The apparatus required is shown in the diagram. (A) Is an efficient wash bottle containing caustic potash solution, which should be renewed frequently. If a rapid flow of air is required it should be supplemented by a second wash bottle. A test should be made to determine the efficiency of the wash bottle; it is essential that the air passing through it should be free from carbon dioxide. (B) Is a decomposition flask as described by Lunge and Machlewski, a Schroetters apparatus or any simple reaction flask. (C) Is a tube containing calcium chloride.




This train of apparatus is all that is required when phosphoric acid is taken to decompose the carbonates in the coal. Phosphoric acid, as suggested by G. S. Morgan (*Proc. Chem. Soc.*, 194, xx., 167) yields results identical with those obtained with hydrochloric acid. When it is thought necessary to use hydrochloric acid, an additional absorption tube (F) must be introduced, containing alternate layers of glass wool and silver

sulphate, in order to eliminate hydrochloric acid. (D) Is a special apparatus (*Analyst*, 1912, xxxvii., 12; *Gas World*, Feb. 22, 1913) the general form of which can be gathered from the diagram. It should not be less than 76 cms. (30in.) in length, and have a diameter of ½in. to 1in., but it should be as small as possible compatible with even working. The inner capillary tube should have an internal diameter of about 1/16in., and be so arranged as to touch the walls and reach to the bottom of the larger tube. The taps of the apparatus should be well ground. In the reservoir (S) there should be sufficient mercury to fill the large tube. (E) Is an ordinary pressure flask, the capacity of which may be from 1 to 3½ litres (usually 2½ litres) The volume of air available for aspirating through the apparatus depends upon the capacity of this flask. Special flasks have been obtained with a ground stopper to which a funnel was sealed, but the arrangement shown which consists of a broad tube, having the inlet closed with a rubber stopper (V) has been found a most satisfactory method for the introduction of the barium hydrate solution into the flask.

*Method of Carrying Out a Determination.*

The flask (E) is filled with fresh air and evacuated by means of an ordinary water pump. The carbon dioxide in the flask is reduced to such an amount as to be negligible. If the percentage of carbon dioxide in the air is known accurately, a correction may be applied for the carbon dioxide remaining in the flask. The evacuated flask is now attached to the special apparatus (D) in the manner shown in the drawing, the taps (M), (H), and (K) being closed. The tap (T) is opened, and the tube of the outlet of the apparatus (D) is placed under the surface of the mercury in the reservoir (S). The tap (K) is then opened, and mercury is drawn into the tube (D) until the column is equivalent to the pressure in the evacuated flask; a record of the height of the column is made, and the tap (K) closed.

The sample of coal is pulverised to pass through a 1/90 mesh sieve, and from 0·5 to 5 grms. are introduced into the decomposition flask (B). This is performed most conveniently by weighing the coal on a piece of smooth copper foil and brushing it into the flask with a camel's hair brush. The coal is covered with about twice its volume (5 to 15 cm.) of distilled water, and is then gently heated, the contents being open to the air, until the water commences to boil, and maintained at a gentle simmer for about 20 minutes. By this means the occluded gases present in the coal are expelled. The flask (B) is then assembled, connected to the train of apparatus, and hydrochloric acid (5 per cent) or phosphoric acid (syrupy diluted 4 times) is placed in the cup (L). The acid is allowed to flow into the coal, the tap (K) is now opened, and (M) opened cautiously until air is drawn through the train of apparatus; the decomposition vessel is gently but efficiently agitated. The rate at which the air passes through the apparatus is carefully controlled, and should be kept constant. There is no necessity to alter the tap (M) once the rate at which the air flows through the vessel has been decided upon. After about 10 minutes, the contents of the decomposition flask are gently heated, the temperature being maintained at about 50° C. for half-an-hour. The liquid is then raised to the boil, and kept at this temperature for an additional 10 minutes. Throughout the whole of this period air is allowed to sweep through the apparatus at the rate of about 2 litres per hour, and any carbon dioxide evolved from the coal is collected in the flask (E). The determination is now complete, and the flow of air is allowed to continue until the train has been completely swept through, or until the pressure in the flask has reached about 70 cms. The tap (T) is then closed, and the flask (E) disconnected. By attaching a freshly evacuated flask, the apparatus is ready for the next estimation.

*Determination of the Carbon Dioxide.*

The method of determination of the carbon dioxide in the flask by means of standard barium hydrate solution, is that described by Pettenkofer the details of which are described in Lunge's "Gas Analysis," but the following is the exact procedure adopted :—

*Preparation and Storage of the Solution of Barium Hydrate.*—The barium hydrate solution is prepared by adding 200 grms. of barium hydrate, and 10 grms. of barium chloride to 1 litre of distilled water. After being allowed to settle, 60 ccm. of the clear supernatant liquid are transferred to an apparatus similar to the one shown (P) and diluted to 1 litre with distilled water. This solution must be preserved from contact with the air, and the apparatus shown is convenient for this purpose. The containing bottle is fitted with an outlet syphon tube, having a narrow capillary (Q); this tube is fitted with a short length (2in.) of india-rubber tubing (R). The use of a small capillary obviates the necessity of having to neglect the large volume of liquid which tubes of greater bore contain before the liquid actually contained in the vessel reaches the pipette. It also possesses the advantage that a pinch cock or bead valve is not required on the india-rubber tubing to prevent the liquid flowing out of the vessel; owing to the narrow capillary there is no tendency for either the liquid to be drawn back into the containing bottle or syphon, or out of it. The second hole in the stopper is fitted with a small tap funnel, which contains first a layer of glass wool, and then about 2in. in depth of fresh soda lime. This is covered with a plug of glass wool, and finally the vessel is closed with a rubber stopper containing a single orifice. The barium hydrate solution has been found to keep very well under the above conditions, and no rapid change of titre will be experienced; at the same time it is desirable to carry out a blank determination upon the barium hydrate solution.

*Method of Titration.*—The tip of the pipette is inserted into the rubber tubing (R), and the required volume of barium hydrate solution drawn off in the ordinary manner. In most of the experiments 50 ccm. were taken for the determination, and when the pipette was filled, the end of it was inserted directly into the rubber stopper (V) of the flask (E). The tap (W) of the flask was then opened gradually, when, owing to its contents being under reduced pressure, the liquid in the pipette is rapidly drawn into the flask. It will be seen that it is possible to repeat these conditions for each succeeding experiment, and as no gas is displaced during the introduction of the barium solution, one of the recognised sources of

error associated with Pettenkofer's method is eliminated. The pipette is removed from the rubber stopper and any traces of barium hydrate remaining behind in the tube are washed into the flask, with distilled water. The contents of the flask may then be brought to atmospheric pressure by connecting the outlet to a wash bottle containing caustic potash. The flask is allowed to stand for half-an-hour with occasional agitation; 1 ccm. of phenolphthalein solution (1 part in 250 ccm. of alcohol) is added, and the liquid rapidly titrated with hydrochloric acid (strength N/20 or N/40) until it becomes colourless. The first discharge of the pink colour is taken as the end-point of the titration. Frequently the pink-colour returns, but this should be ignored. Where a large amount of carbon dioxide is present, and a distinct precipitate of barium hydrate is formed, it is desirable to shake the flask vigorously during the titration, in order to remove any barium hydrate which may be entangled (absorbed) in the precipitate.

The difference between the volume of hydrochloric acid required for the actual titration and that of the blank determination is the volume of acid equivalent to the carbon dioxide present in the flask, and consequently in the weight of coal taken for the determination :—

$$2HCl = CO_2$$

$$1 \text{ ccm. of } N/40\ HCl = 0{\cdot}00055 \text{ grm. } CO_2.$$

The following shows the amount of carbon dioxide found in certain Lancashire coals, from which the white partings (ankerites) had not been separated :—

| Seam | Weight of Coal | Barium hydrate solution ccm | Hydrochloric acid solution N/40. ccm. | Carbon dioxide found grms. | Percentage of carbon dioxide in the Coal. |
|---|---|---|---|---|---|
| 1. Mountain Mine | 5·0 | 50 | 9·2 | 0·0252 | 0·50 |
| 2. Arley ... ... | 3·0 | 50 | 40·2 | 0·0054 | 0·18 |
| 3. Ravine ... | 3·0 | 50 | 33·8 | 0·0107 | 0·36 |
| 4. Abnormal sample, I. ... | 1·0 | 150 | 38·7 | 0·0685 | 6·85 |
| 5. Abnormal sample, II. | 0·5 | 175 | 27·0 | 0·0916 | 18·32 |
| 6. Pemberton, 2ft. | 0·5 | 50 | 42·8 | 0·0036 | 0·72 |
| 7. Garswood, 9ft. | 0·5 | 50 | 45·8 | 0·0022 | 0·44 |
| 8. Hoo Cannel | 0·5 | 50 | 32·4 | 0·0092 | 1·84 |

N/40 HCl (determinations 1 to 6) 1 ccm. = 0·00064 grm. carbon dioxide.

N/40 HCl (determinations 7 and 8) 1 ccm. = 0·000524 grm. carbon dioxide.

*Influence of Prolonged Treatment with Water* (Bayley and Sinnatt)—If the period of heating the coal with water in order to eliminate the occluded gases is continued beyond 30 minutes, only a slight increase in the amount of carbon dioxide evolved could be detected, thus indicating that the period suggested (30 minutes) is adequate.

Five grms. of coal boiled with 20 ccm. of water for 30 minutes: Carbon dioxide found = 0·09 per cent. Allowed to simmer for 6 hours: Total carbon dioxide found = 0·10 per cent of weight of coal. Amount evolved during last 5½ hours = 0·01 per cent of weight of coal.

*The Influence of Using Different Acids* (Bayley and Sinnatt).—The following determinations were carried out under identical conditions upon specimens from the same sample of coal, using hydrochloric acid and phosphoric acid. The results indicate that the two acids yield practically identical results by the method previously described.

Five grms. of coal taken in each experiment :—

| | Percentage of carbon dioxide. Hydrochloric acid. | Phosphoric acid. |
|---|---|---|
| Coal No. 1 ... ... ... | 0·38 | 0·38 |
| Coal No. 2 ... ... ... | 0·27 | 0·26 |
| Coal No. 3 ... ... ... | 1·13 | 1·13 |
| Fusain ... ... ... ... | 0·61 | 0·56 |

The above amounts were found when the coal was digested with the acid for three-quarters-of-an-hour. In the case of No. 1 coal the digestion was continued for further periods, with the following results :—

| Period of digestion. | Carbon dioxide evolved. Hydrochloric acid. | Phosphoric acid. |
|---|---|---|
| First ¾-hour ... ... ... | 0·38 | 0·38 |
| Further 1½ hours ... ... | 0·06 | 0·05 |
| Further 4½ hours ... ... | 0·04 | 0·04 |

We wish to place on record our thanks to Miss P. Wray for help during the preparation of this bulletin.

## THE ALLUVIAL DIAMONDIFEROUS DEPOSITS OF SOUTH AND SOUTH-WEST AFRICA.*

By FRED. C. CORNELL, O.B.E

(Concluded from p. 102.)

UPON the British occupation of the country in 1915, all prospecting and working for diamonds was forbidden, but at a later date, work on a limited scale was allowed. Meanwhile, the occupation had led to thousands of Union troops being stationed on or near the actual fields, and many of these men planned to return when—as was believed to be likely to happen—the country should be thrown open to prospecting. They, and many a river digger looking for more favoured fields, were however, doomed to disappointment for although upon the assumption of the mandate of the country by the Union Government, the bulk of the new territory was thrown open, the coastal belt containing the diamond fields remained forbidden ground.

And to-day the strip of country stretching from the Orange River to the 26th degree of latitude, and from the coast for 100 kilometres inland, including all the richer mines, has passed under the control of a British combine, who will regulate the output and generally manage diamond matters in South-West Africa.

And although this decision has been an extremely sore point with individual diggers, it is probably the best thing that could have happened. For the country, barren, inhospitable, and waterless, is not fit for the individual with small means, and the indiscriminate granting of licences in such a region would probably have led to a great amount of hardship to the many, and riches but to the few.

In conclusion, I may point out that, although an ardent digger myself, and by no means a pessimist, I do not think that anyone should be encouraged to take up the life as long as he can obtain a livelihood otherwise. Certainly he should never dream of migrating to South Africa

for the purpose of doing so. Unless he be exceptionally lucky, the average digging open to him to-day is likely to swallow up all his little capital, and leave him worse off than he would have been in England. On the other hand, it has been abundantly proved of late that the distribution of the diamond is far more widespread than has been imagined, and systematic prospecting may well disclose new fields of far greater richness than those known at present. The startling discoveries in the sands of Luderitzbucht in 1907, may well find their parallel elsewhere; indeed the extraordinary richness of the newly-discovered fields in Akim on the Gold Coast shows that diamonds are by no means even confined to the regions I have described.

DISCUSSION.

THE CHAIRMAN (Major Sir Humphrey Leggett, R.E., D.S.O.), said the author had given a most valuable account of what must be one of the most adventurous and dangerous occupations of the world. His description recalled the poet's words, "Hope springs eternal in the human breast," and showed that man would undertake almost any hardship in the hope of reward. It must have been a surprise, he thought, to some of the audience, to hear how many men were engaged in the industry, and that, during a time of rush, the numbers at a township rose by many thousands. The thought had occurred to him that, in the coming and going across unknown land, although but few people might reap the reward for themselves, not only were most valuable discoveries made in connection with diamonds, but other unsought for discoveries resulted. This adventurous groping also had the effect of bringing to the knowledge of the natives of the districts explored, what a white man and white civilisation really were. The behaviour of the white man in out-of-the-way parts was undoubtedly an example for good. The old lurid stories of what occurred in the mining camps were things of the past. Englishmen in the outlying portions of the Empire behaved as Englishmen should do. It was not always borne in mind how much international politics had been affected by exploration and search for diamonds. Sir Harry Wilson, who was present, would remember that in the old days the boundary between the British territory and the old Dutch Republic turned on a question of where the diamond deposits lay. An extraordinary windfall had come to the British Empire in the acquisition of South-West Africa, and there was a possibility of considerable wealth being extracted from the country by systematic company or individual endeavour. He believed it was a fact that 95 per cent of the diamonds of the world were produced within the British Empire, and that had a considerable influence on international exchanges—for example, it would be a serious thing if the people of England wished to buy diamonds and had to purchase them from the United States, instead of the business being in the reverse direction. It seemed to him, however, that the discoveries which were being made day by day by adventurous people were in need of regulation. He understood from the author that the greater part of South-West Africa was now forbidden to the individual, and he thought the author had done wisely in trying to dissuade individuals from adopting the life of a digger. There could be no doubt that the alluvial diamond industry was of great importance to the welfare of South Africa, and probably other portions of the British Empire as well, and that, under regulation and expert guidance, the end of the discoveries of such wealth was nowhere near.

PROF. ERNEST H. L. SCHWARZ, F.G.S. (Rhodes University College, Grahamstown), said the author had very rightly indicated that geologists did not know very much about the origin of diamonds in alluvial deposits. The subject was an exceedingly difficult one. He remembered being shown at the head office of the De Beers Mine in Kimberley a beautiful octahedron over an inch in diameter, which the experts there said undoubtedly came out of one of the mines in Kimberley, but a digger in the river diggings had brought it in to sell. The detectives at Kimberley identified it as a mine stone, but the digger declared emphatically that it was a diamond from the river diggings. The detectives eventually went out to the claim and dug the gravel themselves, from which they obtained the same kind of diamonds. It was difficult to get over evidence of that sort. He believed the author was correct in saying that the river stones were different from those that were obtained from the mines, but cases occurred in which it was difficult to make such a definite statement. It was not known where the alluvial diamonds came from. For some years past he had been getting washings from sandstones of a considerable age, and he very often found diamond splinters in the concentrates, and diamonds were also obtained from the Witwatersrand conglomerate. It was a possible theory that the diamonds found along the Vaal and Orange Rivers did not come from the mines at all, but from a covering of triassic sandstone. The sand might have been blown away, and the heavy concentrates been washed out of the rivers, the gravels thus being obtained. He endorsed the author's advice that nobody should rush out to South Africa and start diamond digging.

SIR HARRY WILSON, K.C.M.G., K.B.E., in dealing with the administrative aspect of the river diggings, said that when a large shifting population suddenly assembled in a place in which there was no provision for them, naturally the Government of the country had to take certain measures to provide them with the necessaries of organised life. Such instances occurred on the Vaal River on the borders of the Orange River Colony. He remembered on one occasion travelling to see the diggings not far from Christiana, where there was a large collection of river diggers, and Lady Wilson and himself had two or three very interesting days in visiting the whole community. On that occasion diggings were going on in the bed of the River Vaal, some of them of a very elaborate kind. There were also ordinary diggings in various parts of the gravel, and miniature underground mines were being worked in other places by small syndicates of diggers. He desired to endorse what the author had said about the exceedingly law-abiding character of the population, which, coming as it did from all parts of the Union, was naturally composed of very diverse elements. No trouble was ever experienced with the river diggers, and he thought it might be said

that the Administration did their best in the old Crown Colony days to provide them with certain necessaries, for instance, schools, and inspectors and police. He thought the discovery of diamonds near Rouxville must be quite recent, as he did not remember diamonds being found there during his term of office in South Africa. He would very much like to know with what river system it was connected; he presumed it was the Orange River.

MR. CORNELL said that all the diggings were in the old bed of the Orange River.

SIR HARRY WILSON, continuing, said that two very remarkable discoveries of diamonds occurred while he was in the country, one, the Roberts Victor Mine, and the other the Voerspoed Mine, in the neighbourhood of Kroonstad. There was an interesting story in connection with the first mine. An old Cape farmer of the Eastern Province named Roberts continually dreamed that he was going to find a diamond mine, and so convinced was he that the dream would prove to be true that he sold up his property in the Eastern Province and bought a farm in the neighbourhood of Boshof in the Orange Free States. Instead of farming it, he set to work to try and find a diamond mine, but he did not discover one. He eventually died, but in his will he told his executors that they were to carry on the work he had begun, because he was quite certain there was a mine on the property. One of his executors, now Senator Sir John Fraser, employed the best expert he could obtain to carry on the work, and within three or four weeks of the date of his employment one of the richest mines in South Africa was discovered within a very few yards from where Mr. Roberts had been working. Mrs. Roberts leased her interest in the mine for a comparatively short period for a very large sum of money.

DR. M. HORN (Councillor of State, Belgium), said that although diamonds were widely distributed in the Belgian Congo, the only exploitable deposits so far found were the alluvial diamond fields of the Kasai district in the vicinity of the River Tshikapa. These fields were discovered in 1907, and washings commenced in 1913. The efforts of the Administration were first of all devoted to providing this outlying part of the Colony with means of communication. A road about 95 miles long, suitable for motor lorries and oxen-wagons was now leading from Djoko-Punda, the navigable terminus of the Kasai River, to the diamond fields. The output had risen from 50,000 carats in 1915 to 215,000 carats in 1919. The value of the output of 1920 was estimated at £600,000. On the average, the stones were small, but of good quality; the largest stone yet found weighed about 32 carats. The number of natives at present employed on the "placers" was about 8,000, whilst several thousand more were finding employment in providing housing for the white staff and Government officials, road-making, and other constructional work. The Société Internationale Forestiére et Miniére, a little over half of the capital of which the Belgian Congo Government owned, the remainder being divided equally between some Belgian groups and the American banking group of Guggenheim, controlled the undertaking. In view of the rapidly growing requirements of the district, the import trade of the country would be considerably developed, and it would prove, he hoped, a new market for British industry, and at the same time prove of advantage to the owners of the mines, the natives and the Congo Treasury.

MR. J. L WILLIAMS said that the discovery of diamonds in Eastern Akim, to which the Lecturer had referred, was made by the Director of Geology to the Government, who, in the course of his peregrinations for the purpose of building up the geological data of the country, panned some gravels which he thought might contain gold, and found diamonds in addition to gold; and as a result of several days' investigation, discovered diamonds in ten different places. Operations had been conducted in various directions, and diamonds had been obtained with a considerable amount of ease, and an alluvial deposit or a shedding or detrition undoubtedly existed. As the Lecturer had seen the diamonds that had come from it, he would be glad to know whether their appearance indicated the probability of the source being more easily discovered than in South Africa. He believed that at Kimberley the surface discovery consisted of high-grade alluvial deposits which afterwards turned out to be detriton from pipes in the locality. Indications were that plenty of diamonds existed in Eastern Akim, and if those concerned with the development could be informed that the appearance of the stones found there indicated something different from those found in South Africa, it would be greatly appreciated.

MR. W. S. LOCKHART, M.Inst.C.E., said he gathered from the paper that the diamonds in German South-West Africa were mostly of very small size, and it would be interesting to know if any large diamonds had been found, and if so up to what size. He also desired to ask whether if operations were carried on further away from the coast, stones of a bigger weight might be expected to be found. Did the character of the gravel in German South-West Africa coincide with the river digging gravel, and were the diamonds like those obtained from the river digging and the mines?

REAR-ADMIRAL J. DE COURCY HAMILTON, M.V.O. in proposing a vote of thanks to Mr. Cornell fo his excellent paper and lantern views, said he wa glad to know that the diamond-cutting industr had now been introduced into this country an gave employment to a very large number of ex Service men. Although diamonds were wor mainly by ladies, he imagined from the slides tha had been shown that there were no ladies on th diamond fields at all, so at any rate, there was on industry which was left for men exclusively. was a very fortunate thing that Providence ha placed at the disposal of mankind rare metals an stones which were essential to the making ( accurate watches, scales, and compasses.

MR. WALTER REID, F.I.C., F.C.S., in secondir the motion, said that if anybody desired to rea a book which indicated that Britishers were n yet played out, they should read Mr. Cornel' "The Glamour of Prospecting," which was one the finest works of the kind that had ever bee written. As an old prospector in Brazil, he d sired to state that the question of the origin of tl gravel in which diamonds were found was the greatest importance to those connected wi the industry. The reference made in the pap

to the glacial origin was, he thought, quite correct. With regard to the question of the whole of the industry being absorbed by one big company, while that company might make a profit out of the undertaking, that was not the way to develop the industry. The statement had been made that in what was formerly German South-West Africa, nobody might dig or prospect for diamonds. He thought that was shutting down an industry which might become extremely valuable to the country. The question was also of importance to the diamond industry itself. An industry was not necessarily improved by raising the prices, and it must also not be forgotten that some very clever chemists were on the track of the the diamond producer. He knew what had been done in connection with the production of diamonds artificially, and he had made artificial diamonds himself, using carbide as the raw material He had been much struck by a notice which appeared in the Press that the Nobel Dynamite Company of Hamburg, were producing diamonds artificially and had made many thousand carats. That might or might not be true, but the artificial diamond industry might grow as the artificial indigo industry grew. Diamond producers ought to bear in mind that the higher they kept the values the better it paid other people to produce diamonds atrificially.

The Chairman, before putting the motion, said it had been hoped that Sir Bernard Oppenheimer, who had just been honoured with a Boronetcy in recognition of his services in introducing the diamond cutting industry into this country, and thereby given employment to a large number of ex-Service men, would have been present at the meeting. He was sure it was the desire of those present that they should record in an informal way their congratulations to Sir Bernard Oppenheimer on the great honour which had been conferred upon him.

The motion was carried unanimously.

Mr. Cornell, in reply, said the reference Prof. Schwarz had made to stones being found on the Vaal River, which the experts declared to be mine stones, although they were not, was typical of what had happened on more than one occasion, but he maintained the statement he had made in the paper was correct—that there was a perceptible difference between diamonds found on the diggings and those found in the mines. One of the former experts of the De Beers Company possessed an almost uncanny sense of the origin of diamonds. He could not only differentiate between diamonds from the diggings but between the diamonds from various mines. He agreed with Sir Harry Wilson's statement that the Administration was to be commended for the way in which it had handled the populations in the diamond districts, particularly in times of rush, when an enormous population would congregate at a particular place within a very short time. He had been much interested in what Dr. Horn had said with regard to the Belgian Congo. Data had not been obtainable in regard to Belgian Congo diamonds, and he would very much like to get as much information on the subject as possible. It was not easy to dogmatise with regard to the Akim diamonds after merely seeing them in a parcel, but he had formed the opinion that they were not alluvial diamonds, as the term was understood in South Africa. They must have been found within a very short distance of some plug, vent, or form of matrix in the immediate locality. None of the detritus which had been shown him could be called gravel, and, moreover, the diamonds were of quite a different kind from those found in the deposits of South Africa. The stones found in German South-West Africa were very small; in fact, they appeared almost to have been graded because of their extraordinary similarity one to the other, which was not a feature of the stones found on the Vaal River or any of the other diggings in South Africa. An entrancing feature of the diggings proper was that, while one plot might produce a tiny stone, the next plot might produce one the size of a walnut. The diamonds were irregularly distributed, and very irregular in size, varying from hundreds of carats down to minute stones. The largest stones found at Pomona ranged from four to six to the carat, and were all of excellent quality. Those found at Kolmans Kop were smaller still, and as one went farther north so the size of the stones decreased. It was said that one stone had been found at Pomona which weighed 20 odd carats, but it had never been proved to have come from there. The 5,000,000 carats of diamonds that had been produced in German South-West Africa had scarcely produced a dozen stones of a carat weight each. The diamonds were not found in what would be termed gravel, but grit, which had been ground down to the same size as the diamonds found in conjunction with them. With regard to Mr. Lockhart's question as to whether stones of a larger size would be found farther away from the coast, inasmuch as the grading appeared to have taken place by the action of the sea and the wind, and as it was a country in which the whole surface of the ground walked in a storm, it might very conceivably be the case that other deposits of larger stones would eventually be located farther inland. It was not correct, as Admiral Hamilton had inferred, that there were no ladies on the diggings. As a matter of fact, quite a number existed there, and also children, many of the diggers having their wives and families with them. He thought Mr. Walter Reid had missed the point in connection with his remarks that all the diamonds in German South-West Africa were in the hands of a company. He quite agreed that freedom of prospecting was the only possible thing for open countries, but he desired to emphasise that most of German South-West Africa was extremely difficult country. Moreover, not the whole of it was forbidden to the prospector, but only the strip 100 kilometres inland from the sea from the mouth of the river up to the 26th degree. Personally, he was a long way from saying that synthetic diamonds were impossible, but he did not think the average diamond company feared their advent.

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Perphosphates and Their Industrial Application.—Like persulphates, perphosphates are of two distinct types. (1) Perphosphates obtained by electrolysis of a concentrated solution of bibasic phosphate, which correspond to $P_2O_8H_4$. (2) Perphosphates obtained by the action of concentrated hydrogen peroxide on an acid phosphate, and corresponding to the acid $PO_5H_3$, analogous with the mono-persulphuric acid of Caro (P. Ammen Schweiz, *Chem. Zeit.*, 1920).—*Chimie et Industrie*, December, 1920.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

*Ordinary Meeting, February* 17, 1921.

Prof. C. S. SHERRINGTON, President, in the Chair.

THE following papers were read:—

*"A Comparison of Magnetic Declination Changes at British Observatories."* By Dr. C. CHREE, F.R.S.

Field observations of magnetic declination usually aims at supplying not so much the instantaneous value as the mean value appropriate to the place. Unless the observations extend over several days, reference is necessary to the records of a magnetic observatory, and high accuracy is unlikely unless the changes at the field station and the observatory on the day of observation have been closely similar.

The main object of the paper is to investigate the parallelism of declination changes in different parts of the United Kingdom.

A comparison is made of mean monthly, daily, and hourly values as different stations, and of the relative amplitudes of the oscillatory movements which frequently occur on comparatively quiet days. Use is made of magnetic curves from Eskdalemuir, Stonyhurst, Falmouth, and Kew Observatories.

*"The Transmission of Electric Waves around the Earth's Surface."* By Prof. H. M. MACDONALD, F.R.S.

*"The Stability of Fluid Motion."* By Prof. T. H. HAVELOCK, F.R.S.

The object of the paper is to illustrate the use of the criterion, introduced by Reynolds and modified by Orr, as a measure of the degree of stability of various fluid motions under different boundary conditions. After a discussion of the method, some cases are examined from this point of view: they include the flow of a stream with a free surface, and flow between fixed planes under different fields of force and boundary conditions of no slip or no tangential stress or constant normal pressure due to the disturbance from the steady state.

*"Transformation of Integrals."* By Prof. W. H. YOUNG, F.R.S.

*"The Constitution of the Alloys of Aluminium, Copper, and Zinc, containing High Percentages of Zinc."* By J. L. HAUGHTON, D.Sc., and KATHLEEN E. BINGHAM, M.Sc.

The paper deals with the constitution of aluminium-copper-zinc alloys containing not more than 15 per cent of aluminium and 10 per cent of copper. The investigation has been carried out by the study of the heat absorptions and evolutions which take place in heating and cooling alloys between temperatures at which they are liquid and ordinary temperatures; by the measurement of electrical resistance at various temperatures, and by microscopic study of specimens which have been annealed for prolonged periods and quenched, or which have been very slowly cooled and quenched.

From the results obtained a model has been constructed to represent the constitution at temperatures above 250° C., and perspective drawings of this model are given in the paper, as well as a series of isothermal sections and sections parallel to the aluminium-zinc face and to the copper-zinc face. A number of typical photomicrographs are shown.

The diagram advanced by Rosenhain and Archbutt has been used as one face of the ternary prism, the other binary system face being somewhat modified from Tafel's diagram. The ternary system contains an eutectic having a composition of Cu 4 per cent, Al 7 per cent, Zn 89 per cent, the temperature at which it forms—378° C.—being only 2° C. lower than that at which the binary aluminium-zinc eutectic is formed. A binary eutectoidal complex is formed between $Al_2Zn_3$ and the copper-zinc solid solution $\epsilon$. Such a formation is very unusual, if indeed its occurrence elsewhere is known. The line along which this complex is the primary separation from the liquid forms one of the valleys running down to the ternary eutectic; the other two are the depressed aluminium-zinc eutectic and the line separating primary $\epsilon$ from primary $\eta$.

### FARADAY SOCIETY AND MANCHESTER LITERARY & PHILOSOPHICAL SOCIETY.

A JOINT meeting of the Faraday Society and the Manchester Literary and Philosophical Society was held at Manchester on Friday, February 11, 1921.

Sir Henry A. Miers, M.A., D.Sc., F.R.S., President of the Manchester Literary and Philosophical Society, introduced into the chair Prof. Alfred W. Porter, D.Sc., F.R.S., President of the Faraday Society.

Dr. Allan Ferguson, M.A., opened the discussion with the reading of two papers on "Capillarity."

PART I. *"Some General Considerations, and a Discussion of the Methods of Measuring Interfacial Tensions."*

The importance of accurate measurements of surface tensions, in view of the rapidly accelerating development of colloid physics, is becoming increasingly manifest, and a systematic determination of capillary constants is urgently needed. In this paper are discussed the "genetic" relations of various methods for the measurement of surface tensions. A critical comparison of these shows that among the most promising methods for systematic use are those depending on (1) the measurement of large bubbles or drops; (2) the measurement of the maximum pressure required to release a bubble of air from the end of a capillary tube immersed in the liquid; (3) the measurement of the maximum pull on an anchor ring which is immersed in the liquid and slowly withdrawn therefrom.

Some confusion exists as to the conditions under which the equations for the ascent of a liquid in a capillary tube are valid. By a comparatively simple analysis it is shown that, where $a^2$ is the specific cohesion and $h$ the height to which the liquid rises in a tube of radius $r$, the equation

$$2a^2 = rh\left(1 + \frac{1r}{3h} - \cdot 1288\frac{r^2}{h^2}\right)$$

is adequate for all requirements.

Methods are proposed for the measurement of the surface tensions of such liquids as molten metals, and the important problem of the accurate measurement of interfacial tension is discussed.

PART II. *"Modification of the Capillary Tube Method for the Measurement of Surface Tensions."* By ALLAN FERGUSON, M.A., D.Sc., and P. E. DOWSON, M.A.

The capillary rise method for the measurement of surface tensions retains its hold on the affections of experimenters by reason of a somewhat delusive simplicity. In this paper a modification of the method is proposed in which the meniscus is forced down to the end of the capillary immersed vertically in the liquid and the pressure required to effect this is measured on a separate manometer. This simple change sweeps away most of the difficulties attendant on the practice of the ordinary method. Small corrections apart, the difference of level of the surfaces of the liquid in the gauge is equal to the height to which the same liquid would rise in the capillary tube employed. By using a specially light liquid in the gauge, this difference may therefore be magnified. But any manometer of sufficient delicacy may be used, and the use of a catometer avoided. Thus the differential manometer or a simple sloping tube manometer will give accurate results by ordinary naked eye estimations.

Temperature control becomes relatively simple and the temperature of the meniscus may be estimated by means of a thermo-junction placed close to the end of the tube. Calibration of the capillary is unnecessary as measurements are always made with the meniscus in one definite position—at the end of the tube. The following values for the surface tensions of three liquids were obtained by this method :—

Benzene : $T_{15} = 29{\cdot}66$ dyne-cm.$^{-1}$.
Toluene : $T_{15} = 29{\cdot}23$ dyne-cm $^{-1}$.
Methyl propionate : $T_{15{\cdot}5} = 26{\cdot}09$ dyne-cm $^{-1}$.

Prof. A. W. Porter, Dr. F. C. Thompson, Mr. Fry, Dr. A. M. Williamson, Dr. R. S. Willows, Prof. W. W. Haldane Gee, Mr. C. E. Stromeyer, and Prof. Arthur Lapworth took part in the discussion.

A number of manometers were exhibited, including a chattock tilting manometer, and a Threlfall micro-manometer, lent for the occasion by the Cambridge and Paul Scientific Instrument Company.

## OBITUARY.

### PROFESSOR W. ODLING.

THE death of Professor W. Odling on February 17, at the advanced age of 92, removes the last of a small party that used for years to meet monthly at Kensington Park Gardens for the "Water" dinner. Crookes, Odling, and Tidy are three names that for many years were associated with the examination of the London Waters. The "Dinners" were of that cosy character that Crookes used to delight in, and Dr. Tidy, who was a splendid talker, kept the party in a state of uproar the whole evening.

On one occasion the writer very distinctly remembers an explosion of gas that took place in the house about five minutes before the dinner hour. The gas engine that in those early days was used to produce the electric light sprung a leak, filled the engine room with gas, and fired it off, wrecking everything in the basement, and smashing all the crockery in the kitchen; but nevertheless the dinner was held with its usual fund of interest and amusement.

It is not generally known that Prof. Odling as well as Prof. Newlands, was one of the pioneers in attempts to devise a scheme of classification of the elements; he published a paper on the "Natural Groupings of the Elements" in 1857.

Prof. Odling succeeded Faraday as Fullerian Professor of Chemistry at the Royal Institution. He was President of the Chemical Society in 1873-74, and also of the Institute of Chemistry.

## CORRESPONDENCE.

*****The Editor does not accept responsibility for any opinions expressed in this "Correspondence" column. They must in every case be considered as those of the writers.**

### THE CHEMICAL SOCIETY.

*To the Editor of the Chemical News.*

SIR,—In April, 1920, a new set of by-laws proposed by the Council of the Chemical Society were ratified at an Extraordinary General Meeting. It will raise, according to circumstances, either a wan smile or a broad grin on the faces of those who recollect that at the meeting the attendance was 39. The membership of the Society is over 3,500, so that the new by-laws have in fact been imposed upon the Society by 1 per cent of the Fellows, the general body having had no say whatever in the matter. It is very high time that this anomaly was rectified. An improvement has, indeed, now been made in the manner of the election of Council, and in future, the general body of the Fellows will have some say there. But the existing Council took care to neutralise this advantage by inventing a by-law which secures that any proposal to change the by-laws of the Society must still run the gauntlet of a meeting in London at which it is never possible for more than a very small minority of the Fellows—and those almost exclusively resident in London—to be present. If such a proposal is lost there it is lost for good. But should it by some miracle win through (a two-thirds majority being necessary), *then* a poll of the members may be called for—and reaction has another chance. There is no provision for a poll in the other case; what is sauce for the chemical goose is not sauce for the chemical gander. The proper course for the existing Council to have taken was to arrange for the admission of women and for a satisfactory method of electing a Council really representative of the Society, and to leave to that Council the production of new by-laws. It is to be hoped that the provincial Fellows of the Society will be properly impressed by the fact that whilst they have been graciously accorded an opportunity of recording their votes for members of Council on the ballot papers just issued, they have no say on the advisability of altering one of the by-laws, although their opinion might just as easily be obtained on the one subject as on the other.—I am, &c.,

T. S. PATTERSON.

University of Glasgow.

## MANUFACTURE OF FINE CHEMICALS.

*To the Editor of the Chemical News.*

SIR,—We, the undersigned, makers of fine chemicals, extended our research and manufacturing plant at the urgent appeal of the State during the tremendous years that followed 1914, in order to secure those essential products of science without which victory could not be attained. The full record of war-time achievements in the sphere of fine chemicals would read like a romance were the full history disclosed. This key industry is now endangered, and unemployment is rife in it, owing to the flood of imports from abroad which, among other circumstances, the present conditions of the Exchanges makes devastatingly possible. We desire to submit to public knowledge the following facts:—

1. The application of chemical science to industry is a necessary factor for the preservation of our world position in commerce. It is also true to say not only that the chemist and the laboratory are in the first line of national defence, but are pivotal in the development of our industrial and commercial resources and wealth.

2. At very considerable cost, essential plant was erected during the war years, and all of it can now be put to peaceful purposes for the continuance in this country of a fine chemical industry not inferior to Germany's. But, under the present unfair economic circumstances, this plant must become idle and useless, unless the State takes measures for its safeguarding.

3. The fine chemical industry, mobilised and expanded in the hour of the nation's needs, provided during the war—to give a few examples—(a) essential medicinal preparations for naval, military, and civilian hospitals; (b) the higher forms of explosives and gases; (c) photographic chemicals for aerial use; (d) research chemicals, without which the development of many new industrial processes would have been impossible.

4. British science is no whit inferior to that of competing nations, nor are British chemical manufactures inferior in quality.

We feel it our bounden public duty to make known to the country the national importance of an industry which is indeed a key to the unlocking of many doors of economic wealth in the future.—We are, &c.,

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[Continued on p. 120

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## NOTES.

SOCIETY OF LEATHER TRADES CHEMISTS.—A meeting of the British Section will be held at Leathersellers' Technical College, 176, Tower Bridge Road, London, S.E 1, on Friday, March 18, 1921, at 10.30 a.m. In addition to the official business reports will be given as follows:—"Sole Leather Analysis," by Dr. J. Gordon Parker; "Dressing Leather Analysis," by Mr. P. R. Barker; "Chrome Leather Analysis," by Mr. D. Woodroffe; "Tannin Analysis," by Mr G. E. Knowles; "Sulphonated Oils," by Mr. C. F. Barber; "Limeyard Control," by Mr F. C Thompson. The following Officers of the British Section have been elected for 1921: President—Mr. J. R. Blockey; Vice-President—Mr W. R. Atkin; Hon. Treasurer—Mr. C. D. Wilkinson, "Kingshurst," Great Sankey, nr. Warrington; Hon. Secretary—Mr. S. Hirst, 43, Woodbridge Road, Knowle, Bristol; Members of Committee—Prof. D. McCandlish, Mr. J. T. Wood.

## MEETINGS FOR THE WEEK

*Monday, March* 14.

Royal Society of Arts, 8. "X-Rays and their Industrial Applications" by Major G. W. C. Kaye.
Biochemical Society.

*Tuesday, March* 15.

Royal Institution, 3. "Darwin's Theory of Man's Origin" by Prof. Arthur Keith.
Institution of Petroleum Technologists, 5 30.

*Wednesday, March* 16.

Institution of Electrical Engineers, 5.30. "Effect of Electron emission on the Temperature and Anode of a Thermionic Valve," by Mr. G. Stead, M.A. "On some Thermionic Tube Circuits for Relaying and Measuring" by Miss W. A. Leyshon and Dr. W. H. Eccles.
Royal Society of Arts, 8. "Science and the Investigation of Crime" by C. A. Mitchell.
Royal Microscopical Society, 8.

*Thursday, March* 17.

Royal Society, 4.30. "Colour of the Light from the Night Sky" by Lord Rayliegh, F.R.S. "Dissipation of Energy in permanent Ocean Currents, with some Relations between Salinites, Temperatures, and Currents" by R. O. Street. "The Vacuum Arc Spectra of Sodium and Potassium" by S Datta, "Heats of Combustion and Formation of Nitro-compounds" by W. E. Garner and C. L. Abernethy. "Catalytic Dehydrogenation of Alcohols" by E. K. Rideal.
Royal Institution, 3. "The Meteorology of the Antarctic" by Dr. G. C. Simpson.
Chemical Society, 4.
Institution of Mining and Metallurgy, 5.30. (Annual Meeting).
Institution of Electrical Engineers, 6. "The Long-distance Telephone System of the United Kingdom" by Sir William Noble.
Society of Chemical Industry, (At Bristol).

*Friday, March* 11.

Royal Institution, 9. "Researches of a Musical Antiquarian" by Sir Frederick Bridge.
Institute of Metals, 7.30. (At Sheffield).

*Saturday, March* 19.

Royal Institution, 3. "Electricity and Matter" by Sir Ernest Rutherford.

## NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemical Apparatus, &c., for review or notice to be addressed to the EDITOR.

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THE CHEMICAL NEWS.

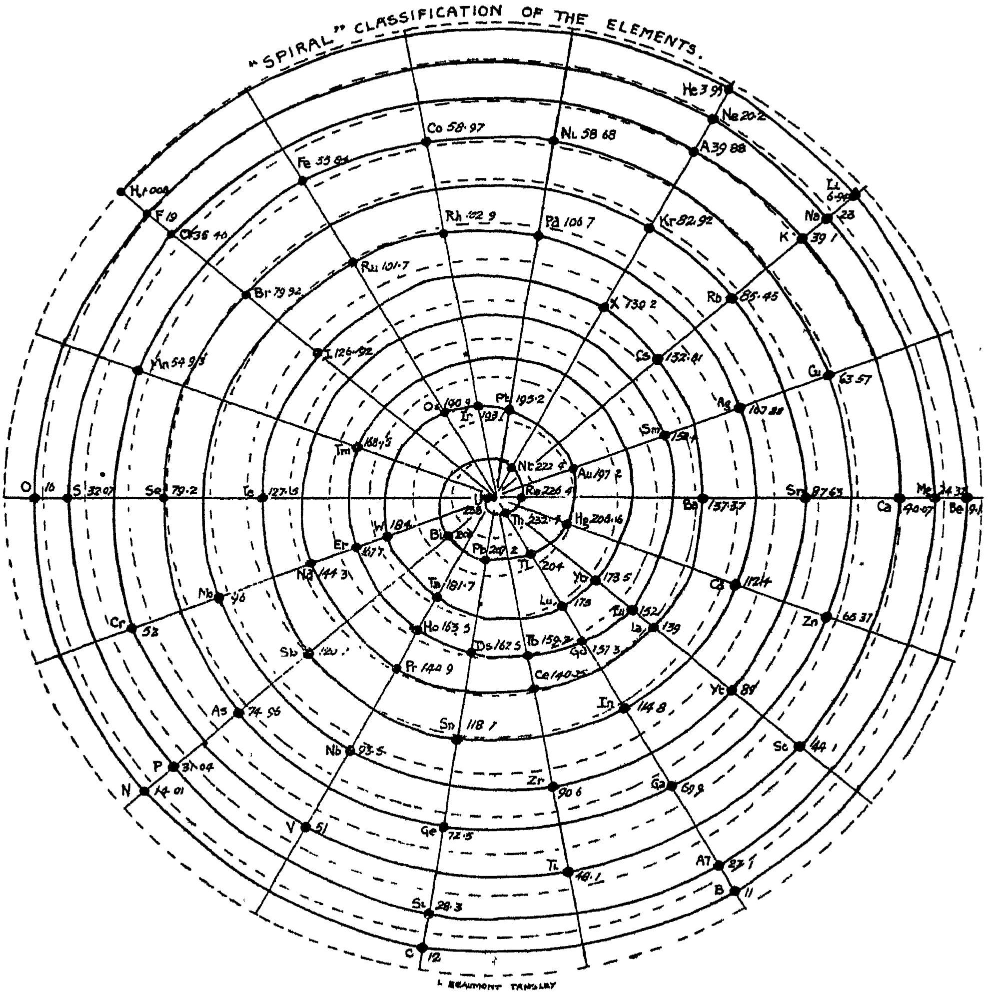
VOL. CXXII., No. 3179.

## SPIRAL CLASSIFICATION OF THE ELEMENTS.

By L. BEAUMONT TANSLEY.

THE drawing shows a simple method of tabulating the elements on the same basis as the periodic classification, but in a way which has less of the uninteresting table, and more of the suggestive evolutionary linking, which would make a greater appeal to the young learner of chemistry than the usual method followed in the textbooks. Continuity is its aim.

The spiral classification can be easily set out by noticing that the 18 sub-groups are allotted 20° each of the complete circle. Concentric circles of increasing radii can then be drawn to any scale to act as a guide to plotting off the exact values of the atomic weights. An increase of one unit for every ten or twenty units of atomic weight will suffice Taking the atomic weight of 240 as centre, the elements are then plotted as they decrease in weight, in (say) a counter-clockwise direction, each being placed on a radial line at its correct value, as given in the International List. Commencing with uranium, a practically perfect spiral will then pass through all the elements until hydrogen is reached, this element being placed at the end of the halogens, since to place it at the end of the alkali metal group, where for many reasons it is often shown, would distort the last convolution of a spiral which is certainly more nearly archimedian than logarithmic.




. The advantages suggested for this means of classification are:—

1. Each group is given equal importance.
2. The elements of each group, while connected by radials, yet never lack companions on either side with properties to a varying degree akin to their own.
3. The muddling "long and short periods" are dispensed with.

4. The "irregular" elements—iron, cobalt, nickel, ruthenium, rhodium, etc.—usually placed as transition elements, for no very particular reason, in an awkward space apart, here fit in naturally.

5. The beginner at chemistry can see that as the atomic weight decreases the groups near the circumference become far apart in properties and position, and are more easily classified than those of high numbers crowded close together at the centre.

6. The rare earth metals can be included without confusion, and fall together in a small area.

7. Ideas can be suggested as to the breakdown of the radioactive metals in a regular way, and the formation of the lighter elements by degradation can be visualized.

8. The "rogue" elements could be brought into line by drawing the spiral with a larger number of convolutions in the same space so that tellurium could be on its correct radial line, but one convolution nearer the centre than iodine on the halogen radial. It might be imagined that on degradation, one complete twist or oscillation of the parent stock gave tellurium only, but in its right order.

9. A great amount of space is left for new elements.

February 6th, 1921.

## AN IMPROVEMENT IN THE NOMENCLATURE OF ORGANIC CHEMISTRY.

By T. SHERLOCK WHEELER, A.R.C.Sc.I., B.Sc., A.I.C.

That the nomenclature of organic chemistry is in urgent need of improvement is admitted by all chemists. A uniform system in which the names of all substances are scientifically connected with their formula is lacking. The Genevan system, in which some effort was made to end the existing state of things has found little favour, perhaps because it did not go far enough. The terminations by which it denotes the various classes of substances have, in most cases, absolutely no connection with the characteristic formula of the class, *e.g.*, the ending "al" denotes a compound containing a carbonyl group linked to a terminal carbon; in other words, a member of the so-called aldehydes.

What is needed, however, is not criticism, but improvement. In the hope that those in the forefront of chemistry may be induced to give the subject the attention it deserves, the following suggestions and outline scheme are very tentatively put forward.

### *Suggestions.*

1. An International Congress, on the lines of the Genevan Congress, to be summoned to draw up a scientific system of nomenclature.

2. The Congress to appoint then a permanent International Committee on the lines of the Atomic Weight Committee. The duties of the Committee to be :—

3. To examine all known types of substances and officially name them on the lines laid down by the Congress.

4. To publish a dictionary in the main European languages, giving the old and new names for each class of substance, and each substance where necessary. To render each name mnemonic, the reasons for its adoption to be given in full.

5. The duty of naming substances to include the naming, on a scientific system, of all reactions and phenomena for which a name is considered necessary.

6. To publish a yearly report officially naming each new class of substance and type of phenomenon discovered during the previous year.

7. A certain number of years to be allowed to chemists to become familiar with the new system. After that, any paper not using it to be refused publication in any journal.

8. All matters of doubt to be referred to the Committee.

During the interval, before the system became compulsory, it could be gradually introduced into the textbooks. Anyone ignorant of the present system, and wishing to consult papers in it, could do so by the aid of the official dictionary.

### *Outline Scheme of Nomenclature.*

The following system seeks to connect the name of each substance with its formula on a simple and consistent plan. The names may appear harsh and unfamiliar at first, but use would soon destroy these objections.

*General.*—Complete saturation is shown by "a," the first vowel. The presence of a double bond is shown by "e," the second vowel. Similarly for "i," the third vowel. Nitrogen, sulphur, and other commonly occurring elements are indicated by their symbols "n," "s," etc., according to the methods described below. Compounds are named either as derivatives of the parent hydrocarbon, or as the derivatives of the parent hydrogen compound of some one element present. Ring compounds and one or two groups are named on a slightly different plan.

*Open Chain Hydrocarbons.*—The paraffin hydrocarbons are called the "HaC" compounds, the number of carbon atoms being denoted by Greek numerals. Methane is monhac, pentane is penthac. The olefines are the "hec" compounds, acetylenes the "hic" compounds. The alphyl radicals are the "ac" radicals methyl, which is methane minus "H," being monac; ethyl diac and so on. In the same way vinyl, which is ethylene less H, is diec. The numbering of chains for the more complicated compounds is on the Genevan plan of taking the longest chain as the basis, *e.g.*, tetramethyl methane is 2·2-dimonac-trihac.

*Halogen Substitution Products of the Hydrocarbons.*—They are named on the Genevan plan Ethylidene chloride is 1.1 dichlordihac. Allyl chloride is 1-chlor-2-trihec, or better 1-chlor-2-(e)-trihac.

*Alcohols.*—Water being the hydro-oxygen corresponding to methane would be "monhao" (or "hao"), and the hydroxy group the "monao" or "ao" radicle. It seems simpler, however, to indicate the hydroxy group by the monosyllable "ho." Ethyl alcohol is then hodihac, allyl alcohol 1-ho-2-(e)-trihac, and alcohols generally the "hohac" compounds.

*Ethers.*—Since ethers are derived from alcohols by replacing H by an alphyl radical, their names are obtained by replacing the "h" of "ho" by "ac," the radical symbol. Ethyl ether is then diac-o-dihac, methyl-ethyl ether is monocodihac,

and the ethers themselves are the "acohac" compounds. In many compounds it will be noted that the final "-hac" may be dropped without causing ambiguity.

*Mercaptans.*—Hydrogen sulphide, the sulphur analogen of methane is "monhas," or more simply "has." Ethyl mercaptan is then asdihac, and the mercaptans the "ashac" compounds.

*Thio-ethers.*—Diethyl sulphide being the ethyl derivative of ethyl mercaptan is diac-as-dihac, and the thio-ethers are the "ac-as-hac" compounds.

*Aldehydes and Ketones.*—Oxygen doubly linked to carbon is analogous to the monhec, *i.e.*, the methylene radical, and should therefore be called the "monheo" or "heo" radical. It is perhaps more convenient to denote it by "oxy." The aldehydes and ketones are then the "oxy-hac" compounds. Acetaldehyde is oxydihac. Acetone is 2-oxy-trihac.

*Acids.*—Acids are the 1-1 hydroxy-oxy compopunds, *i.e.*, the "1.1 ho-oxy" compounds. The numbers are inserted to show that the groups are attached to the same carbon. Acetic acid is 1-1-ho-oxy-di-hac.

*Amines.*—Amines are "HaN" compounds, *i.e.*, they are the hydronitrogen compounds. Methyl-ethyl-propyl-amine is monac-diac-triac-han.

*Phosphines.*—The phosphines are the "hap" compounds.

*Hydrazine and Hydrazines.*—Hydrazine, the hydro-nitrogen analogous to ethane is "dihan." Methyl hydrazine is "monac-dihan," or "dian-monhac."

*Hydoxylamines and Oximes.*—Hydroxylamine being analogous to methyl alcohol is "homonhan," or more simply "hohan." $CH_3.NH(OH)$ is "monac-ho-han"; $CH_3.NH.(OCH_3)$ is "monac-monaco-han."

The divalent radical NH being analogous to monhec, *i.e.*, methylene, is "monhen," or, since no ambiguity can arise, is "hen." Acetaldoxime $CH_3CH:NOH$ is then "hohendihac,," acetketoxime $CH_3C(NOH)CH_3$ is "2-(ho-hen)-trihac."

*Acid Derivatives.*—Acetyl chloride is "1-chlor-1-oxy-dihac." Acetamide is "1-an-1-oxydihac."

*Cyanides and Isocyanides.*—Cyanides, $N:C.R$ are the "NiC" compounds, "i" because of triple bond. Methyl cyanide is nicmonhac. Isocyanides $C:N.R$ are the "CeN" compounds, "e" because of double bond. Methyl isocyanide is cenmonhac.

*Nitro Compounds.*—The nitro group is the di-oxy-nitrogen group; it is accordingly called the "di-oxy-en" group. Nitromethane is then monac-dioxyen. In the same way isomitromethane $CH_2:N(OH):O$ is monhec-ho-oxyen, and the isonitro group is the "ho-oxyen" group.

*Sulphonic acids.*—Similarly the group $.SO_2(OH)$ is the hydroxy-dioxy-sulphur group, *i.e.*, the "ho-dioxy-es" group. Ethyl sulphonic acid is "diac-ho-di-oxyes," ethyl methyl-sulphonate is "monac-diaco-dioxyes," esters being regarded as ether-oxy compounds.

*Cyclo-paraffins.*—Pentamethylene is r penthac, "hac" since it is a saturated compound. The cyclo-paraffins are the "r-hac" compounds, "r" as in the Genevan system, indicating "ring." Another method is to look on pentamethylene as a ring-saturated-carbocyclic-fivemembered compound and its systematic name is then r-a-c-pent. Hexa-hydrobenzene is rachex, and the cyclo-paraffins are the "rac" compounds.

*Saturated Heterocyclic Rings.*—They are named in a similar manner. Piperidine, for example, is r-a-n-hex; ring-saturated-(nitrogen containing)-six-membered.

*Unsaturated Rings.* — Dihydrobenzene is 1.4.di(e)-ran-hex. As in the Genevan system, the position of the double bond is indicated by the number of the carbon from which it starts. In heterocyclic rings the numbering always begins at the non-carbon element. γ-Pyrone is 4-oxy-(double bonds beginning at 2 and 5)-ring-(oxygen containing)-six-membered, *i.e.*, 4-oxy-2.5.di(e)-rao-hex.

*Centric Rings.*—A large number of ring compounds which on valency considerations should be written with double bonds do not possess olefinic properties. It seems best, therefore, to write these compounds with a centric formula, and to read their characteristic properties into that formula, just as we read olefinic properties into a double bond. The names of these compounds are formed by prefixing "c" to the name of the corresponding saturated ring compound. Benzene is c-r-a-c-hex, *i.e.*, centric-ring-saturated-carbo-cyclic-six-membered. Centric compounds, since they do not form addition compounds easily, may be considered as saturated. Pyridene is c-r-a-n-hex, centric-ring-saturated-nitrogen-containing-six-membered. Pyrrol, which may also be written with a centric formula is cranpent. Thiophene, the sulphur analogue of pyrrol, is in a the centric system is a bi-centric-ring-saturated-sulphur-five-membered. Naphthalene, which on the centric system is a bi-centric-ring-saturated-carbocyclic-ten-membered compound, is then bi-c-r-a-c-dec. The Latin numeral is used to avoid ambiguity. Anthracene may be regarded as a tercentric fourteen-membered ring compound. It is therefore called ter-crac-tetradec. Indole is a bicentric nine-membered ring containing one nitrogen atom, and is thus 2-bi-cran-non. The "2" indicates the position of one of the carbons common to the two centres. It is unnecessary to specify the other common carbon, since in nearly all compounds it is in the so-called ortho position to the indicated one. The numbering, it is to be noted, is always clock-wise, but non-adherence to this rule seldom causes ambiguity. Heterocyclic rings containing more than one non-carbon element are named from what may be called the present heterocyclic ring, *i.e.*, the ring containing only one non-carbon element; pyrazole, for example, is 2-N-c-r-a-n pent:—2-nitrogen-centric-ring-saturated-nitrogen-five-membered, the numbering, as usual, beginning at the non-carbon element incorporated in the name.

*Benzene Derivatives.*—As the radical system need never be used in naming the compounds of the above ring systems, benzene excepted, it is not necessary to add "hac" to their names to obtain "ac" for the corresponding radical. In the case of benzene, phenyl could be called crachexac, but it is more convenient to abstract the "h" from the "hex" and to call phenyl "cracex." Benzene derivatives are then named on the same plan as alphyl derivatives; toluene is monac-crachex, and the aromatic hydrocarbons the ac-crahex compounds; phenol is ho-crahex, aniline is cracex-han. As an example of a complicated derivative, *p*-rosaniline $C(C_6H_4(NH_2)1.4)_3OH$ is tri(4.an.cracex).ho.monhac.

*Phenomena and Reactions.*—Tautomerism might be shown by writing the name of the tautomer present in the larger quantity, followed by "t" and an indication of the changes brought about by the link changing. Aceto-acetic ester would be 4monaco.2 4-di oxy-tetrhac-t-[2 (e).2-ho]. The word corresponding to keto-enol is oxy-eho. A better name than tautomerism could no doubt be found for the whole phenomenon. As to the naming of reactions, the Claisen condensation might be called the "oxy-hac" condensation, since hydrocarbon compounds containing an oxy group always take part. Other reactions could be named on similar lines. Terms such as condensation would of course require precise definition.

Substances of doubtful formula would have their names in the official dictionary prefixed by "d" (Latin: *dubium*). Substances of unknown composition could be given a name indicating their class, if known, or if not, a name with a special ending for unknown substances.

The above is intended only as a rough outline of what lines a really systematic system of nomenclature might take. The subject is an important one, and it is to be hoped it will receive the attention it deserves. Should circumstances warrant it, the author hopes to publish later an application of the scheme to more complicated compounds. In the meantime, he would welcome suggestions and criticisms.

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## THE DEVITRIFICATION OF GLASS, A SURFACE PHENOMENON. THE REPAIR OF CRYSTALLISED GLASS APPARATUS.

By ALBERT F. O. GERMANN.

It has generally been supposed that the devitrification of blown glassware in storage or in daily use is a phenomena similar to that studied by Tammann (Tammann, *Z. Elektrochem.*, 1904, x., 532), Guertler (Guertler, *Z. anorg. Chem.*, 1904, xl., 268), and others, which depends on the tendency of a supercooled liquid to form crystal nuclei, from which crystallisation proceeds. Tammann showed that spontaneous devitrification depends on two factors, which seem to be related to the viscosity of the supercooled liquid: the tendency to form crystal nuclei, which increases with the degree of supercooling, though the rate at which nuclei have been observed to form reaches a maximum, and then on account of the damping effect of the diminishing temperature on the speed of formation, rapidly decreases, and for most glasses reaches a value of zero at room temperature; and the speed with which crystallisation proceeds from the crystal nucleus, which for commercial glassware also reaches a value of zero for ordinary temperatures. Tammann has shown that certain substances in solution act catalytically on the formation of crystal nuclei, and that in certain instances the rate may be depressed to zero even in the temperature range of the maximum. This is evidently the ideal condition for chemical glassware, a conditon more or less successfully achieved by glass manufacturers.

It has also been shown (Herbert Jackson, Chemical News, 1920, cxx., 62) that by repeated fusion and solidification supercooled liquids which otherwise devitrify readily can be obtained in the vitreous state. In all cases of this sort that have been studied, water vapour is given off progressively during the process of fusion, and with the removal of it the vitreous state has been found to persist more and more. Subsequent re-introduction of water has been found to promote crystallisation. Herbert Jackson is responsible for the statement that the conclusion seems to be justified that water, and to a smaller extent, carbon dioxide act chemically when many glasses are heated in flames, and that this action plays an important part in the initial stages at least of devitrification. This is undoubtedly true, for it is known that certain glasses, which devitrify very readily in the gas flame, can be worked if heated by radiation. A glass containing barium oxide, which was very stable when heated by radiation in a muffle furnace, quickly devitrified in a gas flame, first becoming grey; under the microscope the grey appearance was shown to be due to the separation of minute bubbles, apparently caused by rapid absorption and subsequent evolution of gases (H. Jackson, *loc. cit.*).

Splitgerber (Splitgerber, *Pogg. Ann.*, 1851, lxxxii., 453) relates his experience with a bit of glass at least 10 years old (most chemists will recall similar experiences): the lenses from a pair of glasses had to be reset, and during the process were heated over a spirit lamp; the surface became roughened and as if frosted over. He showed that this was caused by the driving out of moisture from the glass surface, moisture which was chemically combined. This behaviour is not given by a fresh surface, for a piece whose surface had clouded on heating was ground down and polished, and when again heated showed no clouding.

It has often been noted that glass, under certain conditions, shows efflorescences of sodium hydrogen carbonate on its surface; I have preserved a number of unused test-tubes, imported from Germany before 1914, each of which shows such efflorescences. These tubes all show a marked tendency to devitrify when heated.

It is possible to explain devitrification of chemical glassware as a purely surface phenomenon, unrelated as to immediate causes to the phenomena observed by Tammann.

Much has been said about the surface film of moisture on glass which has come to equilibrium with the atmosphere, but the tremendous affinity of glass for moisture is nevertheless too little appreciated; let me recall an observation made by Moissan that ought to be better known.

"The affinity of dry glass for moisture is so great that carbon dioxide saturated with water vapour at —20° must be passed (through a tube of dry glass containing sodium hydride) for several hours before the gas reaches the hydride in a moist condition" (*Compt. Rend.*, 1903, cxxxvi., 723).

The silicates of which the glass is composed are in equilibrium with this water, and must be more or less hydrolysed, depending on the composition of the glass, so that we may assume the presence of silicic acid, calcium hydroxide, and sodium hydroxide; the bases, however, absorb carbon dioxide from the air, and so are converted to the hydrogen carbonates. The efflorescence is thus directly explained. Washing removes most of

these carbonates. Heating, however, drives off adsorbed moisture, dehydrates the silicic acid, and roughens the surface, depending on the extent of the "weathering" of the glass. The separated silica forms an infusible coating over the surface of the glass, which may under certain conditions dissolve in the underlying silicate, and the surface clear up, or under other conditions yield difficultly fusible calcium silicate, in which case well-defined crystal surfaces may appear (I have preserved a tube of heavy glass which, when heated, developed into what appears to be an excellent example of this sort), the subsequent phenomena being closely similar to the devitrification studied by Tammann and by Guertler, except that crystallisation proceeds from the surface, and not from crystal nuclei on the interior of the mass.

To test the possible correctness of this view, the surface of a tube that had become badly devitrified before the blowpipe was carefully washed with dilute hydrofluoric acid, to remove the separated silica from the surface, and an attempt was again made to work the glass in the flame. The result was remarkable, but entirely in keeping with the hypothesis; as the glass reached the softening point, it became perfectly clear, and could be blown as well as the best new glass. The same result was attained by removal of the surface layers by washing with dilute hydrofluoric acid before heating the glass in the flame, so avoiding any tendency towards devitrification.

At the same time, the older hypothesis, that sodium oxide is slowly volatilised by long continued heating of glass near its softening point must not be lost sight of, for glass which shows no initial tendency to devitrify does so if kept in the flame too long. A common practise has been to reintroduce the lost alkali by some method, but this is always difficult to do. Treatment with hydrofluoric acid, however, is very simple, and thoroughly effective.

At the Morley Laboratory, we have had some difficulty during the past few years in obtaining suitable glass for constructing apparatus for work with gases. Much of Pro. Morley's apparatus remains, but practically all of it devitrifies when the effort is made to work it in the flame. With the new method, however, all of it at once became available for use. Five advanced students, working on various phases of the physical chemistry of pure and mixed gases, each of whom has had to construct his own apparatus, have been able to work without fear of loss through devitrification, which has always been a source of much annoyance to beginners in the art of glass-blowing.

If the devitrification of glass were dependent upon the formation of crystal nuclei upon the surface or within the mass of the glass, a cool storage space would seem to be ideal; my experience has, however, been that glass which had been stored in an attic room under a slate roof for 15 years showed less tendency to devitrify than another lot stored in a ground-floor room of our reinforced concrete laboratory for five years. This is perplexing unless we admit that devitrification depends upon absorption of moisture; the atmosphere of the laboratory has an average humidity much higher than the atmosphere of the attic room, which is in another building. Certain gases present in the atmosphere of a chemical laboratory also seem to play a part, probably acting catalytically; halogen gases, except those containing fluorine, for obvious reasons, seem especially active in this way. A tube which had contained phosgene devitrified badly before the blowpipe; the same tube, after having been exposed casually to the laboratory fumes for more than six months, no longer showed any tendency to devitrify.

*Summary.*

That the devitrification of glass before the flame is a surface phenomenon is shown by the fact that the tendency to devitrify may be removed by rinsing the parts to be fused with dilute hydrofluoric acid, thus removing the surface. Old apparatus which has been broken may be repaired by taking advantage of this fact.

## THE BRITISH GAS MANTLE INDUSTRY.

AMONG the industries that are seeking State assistance through the projected Government Bill relating to "key" industries are the gas-mantle and subsidiary industries. On behalf of these a statement has been presented to the Board of Trade by the Incandescent Mantle Manufacturers' Association, the main points of which are summarised below :—

The Gas Mantle Industry bases its claim to be regarded as a "key" industry upon the following considerations :—(1) Both in time of peace and in time of war incandescent gas lighting is necessary for the adequate illumination of docks, railways, factories, &c. (2) It is estimated that 32 million tons more coal would be required yearly to produce the same illumination if flat-flame burners were used instead of gas mantles. (3) The "stripping" of coal gas has been found necessary to ensure adequate supplies of benzol, toluol, and other hydrocarbons for the manufacture of dyes, drugs, and explosives; such "stripped" gas can only be used as an illuminant in conjunction with the gas mantle. The value of the industry from the standpoints of efficient illumination and coal conservation was recognised by Lord Balfour of Burleigh's Committee on Commercial and Industrial Policy, and recent legislation authorising the sale of gas on a calorific, instead of an illuminating basis has further emphasised the importance of the gas mantle. In Germany the essential nature of this industry, including the raw materials therefor, has been recognised by granting special allocations of coal at the lowest price and supplies of gas which are otherwise restricted.

Before the war, the rare-earth chemicals and the gas-mantle industry were mainly under foreign domination. The total output of Indian monazite sand went to Germany, and British mantle-makers had to purchase thorium nitrate abroad at a price fixed by the Thorium Convention, a combine of German and Austrian manufacturers which was it self controlled by the chief German maker of gas mantles. Further, foreign mantles were sold in this country at prices 2—35 per cent below English factory costs, and 23—70 per cent below the selling prices in the countries of origin. In 1913 foreign importations amounted to between 45 and 50 million finished mantles and over 11 million partly finished (about 70 per cent of our entire

consumption), and the latter were marketed in such a way as to evade the payment of British income tax by the English branch of the German combine, the Auer Gesellschaft. In the same year the English production was 22 million mantles, of which 10 million was made by a company associated with the German combine.

In consequence of this foreign domination the home industry became very precarious; nearly all the factories were running at a loss, wages were low, and employment uncertain and unsatisfactory. Hence, at the outbreak of war, there was insufficient plant to meet the country's requirements, supplies of thorium nitrate were cut off, and there was a shortage of clay rings and other materials required by the industry. To overcome these difficulties the Indian monazite deposits were placed under British control, and five home manufacturers took up the preparation of thorium nitrate, although until the factories were ready the nitrate had to be purchased abroad at arbitrary prices which showed large profits to foreign suppliers. These factories can now produce all the gas mantles the country requires; and during the war they supplied the cerium fluoride and cerium oxalate needed for searchlights and tracer bullets. Prior to the war all the mantle rings required by the home industry were either imported from Germany or supplied by a German-owned company with branch works in this country. These works were purchased by a group of the chief British mantle-makers and so extended that they are now able to meet the country's requirements, although not yet in a position to produce the full range of designs which were offered by the Germans. Ramie yarn, which was also derived from Germany before the war, can now be supplied by British spinning plants in sufficient quantity to meet all requirements.

Owing to the extensions made to buildings and plant (at war prices), and to the establishment of three of four new factories, the output capacity of the home industry is now over 130 million mantles per annum, which is sufficient to leave a considerable surplus for exportation. The following data show the position of the British industry in 1913 and on October 30, 1920:—

| | 1913. | 1919-20. |
|---|---|---|
| Output of mantles ... | 32,000,000 | 82,322,000 |
| Capital employed ... ... | £440,670 | £1,525,710* |
| Workers employed ... | 1,843 | 3,783 |

* Exclusive of £350,000 invested in the thorium nitrate and other subsidiary industries.

The present annual consumption of gas mantles is valued at £1,750,000; £400,000 is paid in direct wages, and at least an equal sum as indirect wages to convert the imported raw materials into the products used by the industry, labour, and wages entering into the cost of the finished article to a degree unusual in other industries. The raw materials used by the gas-mantle manufacturer include thorium nitrate and other chemicals, cotton, ramie, artificial silk, asbestos yarns, clay rings, and cardboard boxes. At the present time there is grave stagnation in the above trades, which is mainly due to the increasing importation of foreign mantles (over 10 million in 1920), and the prospect of further competition at prices below British manufacturing costs. The low prices of foreign mantles are the result of :—(a) Attempts by foreign makers to recapture their former markets at any cost; (b) the low rate of foreign exchanges; (c) longer working hours in foreign factories (60 hours or more per week compared with 48 in this country) and the lower standard of living of the worker; (d) large pre-war stocks of certain raw materials held by German manufacturers. The British consumer is not obtaining the full benefit of the lower prices, as the intermediate profit is mainly retained by the importers and dealers. The Labour representatives on the Joint Industrial Council for the industry proposed a resolution, which was passed unanimously, deploring the increasing importation of foreign mantles, and urging the Government to take steps to counteract the effects due to foreign rates of exchange. At the present time some of the British factories are closed down, and the rest are working short time; manufacturers are carrying large stocks at a season when demand normally exceeds the rate of production; employment in the industry is declining, and generally the situation is so serious that immediate action is imperatve. In concluson, it is submitted that the manufacture of thorium and rare-earth salts, incandescent mantles, and clay rings, be recognised and assisted as "key" industries; that legislation be introduced forthwith to protect the British worker against unemployment resulting from foreign competition; and that the British manufacturers who have responded to appeals to lay the foundations of a self-supporting industry be assured a market free from unfair competition.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

*Ordinary Meeting, February 24, 1921.*

PROF. C. S. SHERRINGTON, President, in the Chair.

THE following papers were read :—

"*A Remarkable Flint Implement from Selsey Bill.*" By SIR E. RAY LANCASTER, K.C.B., F.R.S.

The implement described, and depicted in four careful wash-drawings of the natural size, together with two hammer-stones obtained with it, was found resting with other large broken flints on a bed of clay underlying "the Coombe rock gravel," and exposed by tidal action on the shore of Selsey Bill, by Mr. Edward Heron Allen, F.R.S., in 1911. It is remarkable for its large size, being eight inches long and weighing 5lb. 9oz. It is of rostrate form, with a convex dorsal and flat ventral surface, and has been shaped by powerful blows, resulting in coarse flaking of undoubted human workmanship. It belongs to a very early palæolithic horizon, probably "pre-Chellean." The only flint implements of similar weight and size known are two also of very early (viz., Upper Pliocene) age. One is from the Suffolk bone-bed, 8¼lb. in weight, and is figured in the *Phil. Trans.*, B, ccii., 323, 324; and one weighing 7lb. 6oz. was discovered last September by Mr. Reid Moir with a large number of remarkable "worked" flints on an ancient workshop floor beneath the forest-bed at Cromer. The question is raised as to how such unwieldy implements could be handled and for what purpose. It is suggested

that the race of men who made and used them had larger hands and more powerful limbs than have more modern races.

"*Regeneration and Reproduction of the Syllid Procerasta.*" By E. J. Allen, D.Sc., F.R.S.

*Procerastea Halleziana* was found living in membranous tubes on the stems of the hydroid Syncoryne. The worm was observed to feed by piercing the body-wall of the hydranths with its extruded pharynx and pumping out the contents of the gastral cavity of the hydroid. The proventriculus of the worm functions as a quick-acting pump, making from 150 to 200 pulsations a minute.

Sexual reproduction in Procerastea is quite similar to that in Autolytus, each individual forming a single large stolon (with stolon-head on segment 14), which is set free as a male Polybostrichus or a female Sacconereis, before a second stolon is produced.

In addition to sexual reproduction, the procerastea were found to be undergoing rapid multiplication by a process of asexual reproduction, consisting of fragmentation, followed by the regeneration of anterior and posterior ends.

Fragmentation can be induced by artificial means, and takes place in a definite way. The head and first seven setigerous segments form the first piece. This is followed by three sections, of two segments each; these by three sections, of three segments each; and these by four or five sections, of four segments each. Behind these, sections of three segments reappear and are continued to the pygidium.

Experiments showed that the rate of regeneration of the different sections varied according to the region of the body from which they came, being most rapid in those from the middle region.

Regeneration of anterior segments appears to continue until the original segments come to occupy exactly the same position in the regenerated worm as they had occupied in the parent, and then stops. Posterior regeneration was more active when the original segments came from the anterior end of the parent worm. The posterior portion of a female stolon regenerated a complete *souche* of 13 segments, and had commenced to regenerate a stolon-head when it was found.

"*The Enzymes of B. coli communis.* Part II.—(*a*) *Anaerobic Growth followed by Anaerobic and Aerobic Fermentation.* (*b*) *The Effects of Aeration during the Fermentation.*" By E. C. Grey and E. G. Young.

Section A.—Anaerobic fermentation of glucose by an emulsion of *B. coli communis* proceeds differently according as the organisms have been grown previously with or without oxygen.

When the immediate past history has been anaerobic, the fermentation under anaerobic conditions yields very little or no lactic acid and greatly diminishes succinic acid. In place of these, acetic acid appears in large proportion. Admission of oxygen during the fermentation leads to lactic acid production. The fact that acetic acid replaces succinic acid entirely gives additional proof of the close relationship of these two substances.

The results also confirm the conclusions of the earlier sections as to the independence of the lactic acid, acetic acid and probably of the carbon dioxid fermentations.

Section B.—The effect of introducing oxygen in the fermentation of glucose by *B. coli communis* is to increase the lactic, acetic, and succinic acids, and to diminish the hydrogen, carbon dioxide, and formic acid, but to leave the alcohol unchanged.

Under anaerobic conditons greater variations occur in the proportion of alcohol to acetic acid than under aerobic conditions, and it would appear that one of the effects of the introduction of oxygen during the fermentation is to inhibit the mechanism of auto-reduction, which is responsible for the variations in alcohol when such occur.

Contrary to expectaton, the products of aerobic fermentation contain not more, but less, oxygen than the corresponding products of anaerobic fermentation of glucose; but there is a gain of oxygen in both cases upon the original glucose. If, as seems likely, this extra oxygen comes from the water, then it would appear that one of the effects of the introduction of oxygen is to diminish the part played by water in the reactions.

"*Anthocyanins and Anthocyanidins.*"—Part IV. By A. E. Everest, D.Sc., and A. J. Hall, B.Sc.

The paper deals with the constitution of the blue anthocyan pigments in flowers and with the manner in which anthocyan pigments are formed in Nature.

The conclusions of Shibata, and Kasiwagi, concerning the constitution of the blue anthocyan pigments in flowers are compared with those of Willstätter and Everest. Evidence is produced which indicates important differences between the complex salts known to be formed by the anthocyan pigments (and other pyrylium compounds) with the salts of such metals as iron and the blue pigments present in flowers. Reasons are given for concluding that such of the blue plant pigments of this group as have been investigated do not belong to the former series, but are probably comparable to the alkali phenolates of the flavonols.

Evidence is produced which considerably strengthens the conclusion, already expressed by Keeble, Wheldale, Everest, and others, that in plant synthesis the flavonols are first formed, and from them the anthocyans—not *vice versâ*.

## PHYSICAL SOCIETY.

*February* 25, 1921.

Prof. Sir W. H. Bragg, F.R.S., President, in the Chair.

The following papers were read:—

"*A Note on the Hot Wire Inclinometer.*" By R. H. Humphrey.

Two fine platinum wires were stretched parallel to each other in a hole in a copper block, and were heated electrically in a Wheatstone bridge arrangement. The changes caused by rotation were investigated with hydrogen, air, and carbon dioxide surrounding the wires. It was found that both for the same current, and for the same temperature of the wires, the inclinometer filled with carbon dioxide was much more sensitive than one

filled with air. The shape of the curves obtained suggests that the temperature gradient in the region traversed by the wires is nearly uniform, the difference of temperature of the layers of gas in which the wires happen to be being sensibly proportional to the vertical distance between them.

DISCUSSION.

Dr. J. S. G. THOMAS said that the conditions under which the author's experiments were carried out made the results quite incomparable with those described in his own paper on the subject. In his experiments the free convection was of much greater importance than the conduction loss, whereas in the present paper the arrangement of the apparatus was such that conduction preponderated. For example, the wires were much too near the walls of the containing chamber. The statement that for the same current the effects in carbon dioxide are greater than in air is exactly what would be expected if conduction predominated, but was opposite to what happened in his experiments in which convection predominated. In the latter case, the specific gravity and specific heat entered into the problem. He had made a calculation of the heat loss by conduction in hydrogen, air, and carbon dioxide, using King's formula, and found these to be in the proportion of 12 : 100 : 200. From Fig. 3 we find that the heat losses in the author's experiments are very closely in this ratio, which bears out the conclusion that conductivity was the predominant factor. The temperature of the wires in the experiments of Fig. 3 should be stated. Another difference between the author's experiments and his was that the wires were too far apart to bring the joint effect due to shielding of the second wire by the first into play.

Mr. J. GUILD said it was of interest to him that so many workers seemed to have taken up the somewhat obvious suggestion he had made, in discussing Mr. Thomas's paper, of investigating the temperature distribution in the neighbourhood of a hot body by means of the interferometer. He would like to give a word of caution in connection with the method, which was that the contour fringes observed would only be true isothermals if the wire were infinitely long in the direction of vision. In ordinary conditions a slight correction for end effects would have to be made in obtaining quantitative data from the fringe system.

Mr. F. E. SMITH asked if experiments had been made at different pressures.

Mr. HUMPHREY, in reply, said he was fully sensible of the truth of Dr. Thomas's remarks about convection and conduction. With regard to the experiments of Fig. 3, the temperature of the wire was 130° C. to 140° C. in each case. He had not noticed that the figure gave ratios so close to those given by King's formula. As regards the mutual influence of the wires, the region to which the effect of the upper wire extended could be very easily seen from the interferometer experiments. In reply to Mr. Smith, he had not experimented at different pressures.

*"The Magnetic Susceptibility of Certain Natural and Artificial Oxides."* By PROF. E. F. HERROUN and PROF. E. WILSON.

(1) The susceptibility of ferric oxide, as occurring in nature, varies through a wide range, but in the case of artificial preparations the range of variation may be much greater.

(2) The highest susceptibility exhibited by artificial ferric oxide occurs when either ferrous or magnetic oxide is oxidised at a high temperature in the anhydrous condition. From hydrated magnetic oxide the susceptibility, though considerable, is much less.

(3) The lowest susceptibility is obtained from native hæmatites, or naturally oxidised chalybite, or by the ignition or precipitation of ferric salts.

(4) It appears that the passage through the stage of magnetc oxide impresses more pronounced magnetic properties upon the resutling ferric oxide.

(5) The actual values of susceptibilty have been obtained in the case of ferrites, one of the most conspicuous being that of copper.

(6) Heating feebly magnetic ferric oxide with a basic oxide, *e.g.*, lime or magnesia, increases susceptibility (confirming List and others).

(7) When higher susceptibility has been produced by heating ferric oxide with a basic oxide such as that of silver or mercury, subsequent removal of the metal leaves the ferric oxide in a magnetic condition.

(8) The chemical compounds (aluminates) formed when ferric oxide is replaced by alumine oxide show no definite increase in susceptibility, which is in marked contrast with the ferrites.

DISCUSSION.

PROF. BRAGG showed a model of the molecule of magnetite as deduced from its X-ray spectra, and pointed out various conclusions which could be drawn from it. For instance, it was impossible to deduce the properties of the magnetite from those of $Fe_2O_3$, and FeO, nor could any of its properties be ascribed to one or the other, because the crystalline form of the $Fe_2O_3$ and FeO in the magnetite molecule differed from their crystalline form when separate. It was possible by X-ray spectroscopy to say what crystals were present in any powder. No doubt magnetic effects were associated with the crystal structure; but experiments on Pyrrotine showed no difference between the magnetised and unmagnetised state.

DR. RAYNER asked if differences in aggregate form rather than in crystal form might not account for the different magnetic properties of some substances of the same composition.

PROF. WILSON said he was disappointed by Prof. Bragg's remark about Pyrrotine, as it partially answered the question he wished to ask. Would the X-ray spectroscope be likely to show any difference in the two ferric oxides of such widely different susceptibilities mentioned in the paper?

PROF. BRAGG: If there is any difference in crystal structure it would show it.

MR. GUILD said the case of Pyrrotine was different from that of the two ferric oxides. The experiment with Pyrrotine showed that there was no difference in the molecular structure of a magnetisable substance when magnetised and unmagnetised. This one would expect since the phenomena of magnetisation are accounted for by the orientation of the molecules, and not by any alteration of their properties. The case of the two ferric oxides in which Prof. Wilson was interested was quite different. Here we had magnetisable and non-magnetisable modifications of

the substance. In this case one would expect to find a difference in molecular structure revealed by the X-ray spectrometer.

DR. J. S. G. THOMAS asked if the differences might not be due to differences in the magnetic coupling of the electrons.

PROF. BRAGG: That is the problem we are all working at. In the case of the diamond there is no doubt that the carbon atoms point in opposite directions.

PROF. HERROUN said that in Pyrrotine the susceptibility in one direction was 70 times that in another. Would the X-ray spectra give any clue to this?

*"The Refractometry of Prisms."* By J. GUILD.

In this paper a generalised formula for the refraction of light through a prism is obtained, and the particular cases pertaining to practical methods of refractometry deduced from it. The sensitivity of various methods for various prism angles and refractive indices is shown in a series of curves as is also the liabilty to error due to errors in auxiliary constants.

DISCUSSION

MR. T. SMITH agreed that information such as that in the paper would help to dispel the illusions concerning the accuracy of their observations which most workers on refractive index measurement seemed to possess. He had had occasion to analyse results supposed to be the last word in accuracy, but had found quite serious errors in many of them.

He would like to see the general adoption of some system of angular notation such as that used in the paper. The only case which presented difficulty was when applying it to a system in which there were reflecting as well as refracting surfaces. He had found it convenient in such cases to keep to the angle convention, but to change the signs of the refractive indices after reflection.

DR. D. OWEN said the author had been speaking of tolerances of a few seconds. As a rule one felt satisfied when one got angles correct to a minute. What was the accuracy in angle which the author considered should be attained in precise measurements?

MR. GUILD said that accuracy in angle measurements was largely a matter of choosing proper methods and apparatus. For the cases most frequently met there was no great difficulty in measuring to a second provided the surfaces of the prism were such that this accuracy had any meaning. He was at present experimenting with a very cheap and simple arrangement with which he hoped to reach a tenth of a second in cases which were fit for such precision.

*"Tracing Rays through an Optical System."* By T. SMITH.

The paper, which is mainly mathematical, is a further development of the system described by the author in the previous papers of the same title presented to the Society; formulæ for skew rays are put into shape as far as possible similar to those applying to rays in one plane.

## INSTITUTE OF CHEMISTRY.

*Forty-third Annual General Meeting.*

SIR HERBERT JACKSON, the retiring President, in the course of his Address, remarked that Government Departments and official authorities generally had shown more inclination in recent times than in the past to accord higher recognition to the services of men of science. The conditions of appointments of chemists, both in the Government service and in industry had been improved, and until the close of 1920 the profession had been in almost a unique position in that very few indeed of its members were disengaged. The prevailing depression in industry had had some effect on the employment of chemists, but even now less than 50 were disengaged out of nearly 3,300 on the Roll The By-laws of the Institute had undergone revision to provide for the representation of chemists from various parts of the country and practising in different departments of work, and alterations had been made to define more specifically certain points relating to the ethics of the profession and further to restrict the membership of the Institute to British subjects. The Institute was taking part in many matters affecting the public life of the country where chemistry was concerned, and the Annual Report showed that chartered professional bodies of this character were able to render the State valuable service. The greater consideration given to science by the Government was an encouragement to the coming generation of chemists to follow a career of essential and vital importance to the needs of the country. It would probably be regarded as desirable at the present moment for the Council of the Institute, without taking part in politics, to give expression to their views on the grave importance of maintaining in this country industries on which not only the future development of our chemical industry and many allied industries depends, but the future of a very large number of students of chemistry who are now in the course of training. The Institute was entrusted by its Charter with securing the supply of well-trained chemists, but unless a great chemical industry was maintained there would be a very poor prospect for them. The President maintained that the Institute had throughout its existence fulfilled the purposes for which it was incorporated. It had kept alive the corporate spirit of the profession, the means whereby the opinions and views of its members found expression in matters of public concern. It was the officially-recognised public body to whom the country could turn for advice and guidance on matters relating to the profession. It rendered every possible assistance to those who intended to follow the profession of chemistry, and promoted and maintained the highest standard of training and competence for that profession. It registered the trained and competent and thereby supplied competent professional service for the country. Moreover, it promoted the strictest integrity on the part of its members in their dealings with one another and with the public, and fostered by every means in its power the status of the profession. He was confident that it would continue to gain strength and prestige

Mr. Alfred Chaston Chapman, F.R.S., succeeds Sir Herbert Jackson as President. The Officers

and Council were elected as nominated and the Censors and Auditors were elected for the ensuing year. *President*—Alfred Chaston Chapman, F.R.S. *Vice-Presidents*—Horatio Ballantyne, Ernest Mostyn Hawkins, Sir Herbert Jackson, K.B.E., F.R.S., William Macnab, C.B.E., Gilbert Thomas Morgan, O.B.E., D.Sc., F.R.S., George Stubbs, C.B.E. *Hon Treasurer*—Edward William Voelcker, A.R.S.M. *Members of Council*—Walter Ernest Adeney, D.Sc., A.R.C.I. (Dublin), Wm. Bacon, B.Sc. (London), Francis Howard Carr, C.B.E. (London), Arthur Jenner Chapman (London), Allin Cottrell, M.Sc. (Oldham), Alexander Charles Cumming, O.B.E., D.Sc. (Edinburgh), Frederick George Donnan, C.B.E., F.R.S. (London), Lewis Eynon, B.Sc. (London), Alexander Findlay, M.A., D.Sc., Ph.D. (Aberdeen), George Watson Gray (Liverpool), Frank William Harbord, C.B.E., A.R.S.M. (London), Charles Alex. Hill, B.Sc. (London), Patrick Henry Kirkaldy (London), Frederic Herbert Lees (London), Samuel Ernest Melling (Manchester), Gordon Wickham Monier-Williams, O.B.E., M.C., M.A., Ph.D. (London), Harold Moore, O.B.E., B.Sc. (London), Andrew More, A.R.C.S. (London), Frederic Mollwo Perkin, C.B.E., Ph.D (London), Benjamin Dawson Porritt, M.Sc. (London), Thomas Slater Price, O.B.E., D.Sc., Ph.D. (London), William Rintoul, O.B.E. (Ayrshire), William Henry Roberts, M.Sc (Liverpool), John Rogers, O.B.E. (Glasgow), Ernest Woodhouse Smith, D.Sc. (London), Leonard Ellerton Vlies (Manchester), Sir James Walker, C.B.E., F.R.S. (Edinburgh).

## SOCIETY OF PUBLIC ANALYSTS.

*March* 2, 1921.

Mr. Alfred Smetham, President, in the Chair.

A Certificate was read for the first time in favour of Mr. Percy N. Mould.

Certificates were read for the second time in favour of Messrs. Jules Cofman-Nicoresti, Walter K. Fletcher, William Singleton, Francis G. H Tate, James Darnell Granger, Ph.D., F.I.C., Ed. B. Maxted, Ph.D. (Berlin), B Sc., Russell G. Pelly, F.I.C.

The following was elected a member of the Society: Mr. W. R. Schoeller, Ph.D.

The following papers were read:—

"*The Acidity of Ink and the Action of Bottle Glass on Ink.*" By C. Ainsworth Mitchell, M.A., F.I.C.

The author gave the reason for the addition of acid to ink and the amount present in standard inks. He described acid-free inks, the estimation of acidity and the difficulty caused by dye-stuff. The hydrogen peroxide method was dealt with, its limitations and uses, and the estimation of total acidity as a check on the manufacturing process. Lastly, the author described the various effects of glass on ink. A number of exhibits were shown.

"*The Detection of Adulteration in Butter by Means of the Melting-Point of the Insoluble Volatile Acids.*" By George Van B. Gilmour, B.Sc., A.R.C.Sc.I., A.I.C.

The author described how small amounts of coconut and palm-kernel fats added to butter lower appreciably the melting-point of the insoluble volatile acids Tables of melting-points and distillation figures for pure fats and mixtures were given, also graphs showing how the melting point is affected when increasing quantities of coconut and of palm-kernel fat are added.

"*Method and Apparatus for Routine Determination of Melting-Points of Fats and Fatty Acids.*" By S. H. Blichfeldt and T. Thornley.

The authors describe how a column of melted fat 1 cm. long in a tube of 1 mm. bore, 3 mm. diameter, and 60 mm. long, is rapidly solidified on ice, and kept on ice during two hours; it is then placed in a water-bath with the upper level of column 1 cm. below the surface, and heated at 1° C. per minute. The temperature at which the column rises is noted as M.P. The apparatus is a rectangular glass water-bath holding 20 tubes, and arranged for electrical heating, stirring, and lighting.

## NOTES.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 7th inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Sir Frank Benson, Mr. I. W. Bullen, Mrs. R. C. Bussell, Miss. E. Caird, Mr. C. H. Combe, Mr. H. R. Darlington, Mr P. Faraday, Mr. G. J. Goldie, Major Gordon Home, Mr. W. G. Klein, Dr. A. G. Levy, Miss J. Lindley, Mr. E. MacRury, Mr. M. R. Trower, Mrs. Ractivand, Sir Robert Robertson, and Miss L. C. Western were elected Members. The Secretary reported the deaths of Professors Odling and L. C. Miall, and resolutions of condolence with the relatives were passed.

Royal Institution.—The following the the Lecture arrangements at the Royal Institution after Easter: Professor R. A. Sampson on (1) "The Nebular Hypothesis," (2) "Measurement of Starlight"; Dr. Keith, four lectures on "Darwin's Theory of Man's Origin"; Mr. Clodd on "Occultism"; Sir James Frazer on (1) "Roman Life (Time of Pliny the Younger)", (2) "London Life (Time of Addison)"; Dr. C. T. R. Wilson on "Thunderstorms" (the Tyndall Lectures; Mr. H S. Foxwell on "Nationalisation and Bureaucracy"; Dr. C. S. Myers on "Psychological Studies—(1) Localisation of Sound, (2) Appreciation of Music"; Mr. D. S. MacColl on "War Graves and Monuments"; Sir Alexander Mackenzie on "Beethoven"; Dr. H. H. Dale on "Poisons and Antidotes"; Mr. H. Y. Oldham on "The Great Epoch of Exploration—(1) Portugal, (2) Spain"; Mr. C. C. Baly on "Chemical Reaction"; Mr. F. Legge on "Gnosticism and the Science of Religions"; and Dr. R. S. Rait on (1) "Scotland and France", (2) "Scott and Shakespeare". The Friday evening meetings will resumed on April 8, when Dr. R. H. A. Plimmer will deliver a discourse on "Quality of Protein in Nutrition." Succeeding discourses will probably be given by Mr. Ernest Law, Sir James Walker, Sir Frank Dyson, Astronomer Royal, Sir Robert Robertson, Dr. Bateson, Dr. Starling, Mr. A. Mallock, Dr. Leonard Huxley, Dr. A. G. Webster, Sir J. J. Thomson, and other gentlemen.

TETRALINE IN MANUFACTURE OF LAKES AND VARNISHES.—The varnish substitutes employed during the war in Germany were far from satisfactory. However, those with base of teraline, alone or mixed with other usual solvents, were so. The dissolving action of various tetralines were vari-made. For example, varnishes are made by preparing a saturated solution of lake in tetraline and diluting it with a miscible solvent with a slight lake-dissolving power and more rapidly volatilised than tetraline Such a varnish allows of a second coat without softening of the first. Tetralines have a slight odour of camphor which can easily be masked by adding a little spirit of turpentine.—*Industrie Chimique*, January, 1921.

TECHNICAL COLLEGE, BRADFORD.—A course in Public Health, designed to meet the needs of qualified medical practitioners who may wish to obtain the Diploma in Public Health of the Royal College of Physicians of London, and Surgeons of England, has been arranged by the Technical College Committee and the Health Committee of the City Council. For this purpose the Technical College has recently been placed upon the list of recognised Institutions by the Royal Colleges. The proposed course will extend over 25 weeks, and will include lectures and laboratory work in bacteriology and pathology, and in chemistry. The course in bacteriology will be conducted in the Public Health Laboratories. In connection with this work, Dr. William Campbell has been appointed Lecturer in Bacteriology and the Pathology of Industrial Diseases, and Dr. R. Cecil Robertson has been appointed Assistant Lecturer and Demonstrator in Serology and Immunology in the College. Both gentlemen are members of the permanent staff of the Bacteriological Laboratories. The course in Chemistry, which will be under the direction of the Head of the Chemistry Department of the Technical College, Dr. R. D. Abell, will be conducted in the Chemical Laboratories of the College. The recognition of the College for post-graduate work of this nature marks an important point in the development of the work of the College. The extension of the post-graduate section of the work of the College is receiving ample attention, and increasing provision for this work in the College is now being made

ACTION OF CHLOROPICRINE ON THE GERMINATIVE FACULTY OF SEED.—Experiments made by M. E. Miège demonstrate that parasitic insects on seed can be destroyed by chloropicrine in 24 hours, utilised in the proportion of 15 to 20 cubic cm. per cubic metre of seed. Longer contact and larger quantities seem useless. The action of chloropicrine on seed varies with the species of seed, the percentage employed and the duration of treatment. Imperceptible on some (leguminous, linseed, &c.), it affects on the contrary the germinative faculty and energy of others (hemp, beet, and especially cereals). This unfavourable influence generally increases with quantity, and the length of time of treatment. In the conditions required for disinfection it may decrease the germinative power of wheat 30 per cent, and larger quantities are yet more noxious. On the contrary, the seed of leguminous plants is absolutely immune.—*Comptes Rendus*, January 17, 1921.

NEW PROCESS FOR MANUFACTURE OF SUPERPHOSPHATES.—A mixture of phosphorite, lime, and silica is heated to nearly the point of fusion. In these conditions a lime-silicite is formed which takes one or two molecules of lime from the tri basic phosphate of lime. The phosphate is thus brought to the mono or bicalcic state, and consequently soluble with organic acids.—*L'Engrais* January 7, 1921.

FERTILIZING ACTION OF SULPHUR.—Experiments made by M Nicolas demonstrated that besides the important qualities ascribed to sulphur, both as an aliment in form of sulphuric acid and catalytic agent in assimilation of nitrogen of the soil, there is also its nfluence n fixaton of atmospheric carbon owing to its action on chlorophyll. Thus its employment in agriculture deserves exhaustive researches.—*Comptes Rendus*, January 3, 1921.

REPORT OF IMPORTS AND EXPORTS BY AIR IN 1920.—The Air Ministry states that the value of imports and exports by air during 1920 exceeded a million pounds, the respective amounts being £677,047 and £339,108 and the grand total £1,016,155. For the last quarter of the year the value of imports and exports conveyed by aircraft were approximately four times greater than for the same period of 1919, although there was a reduction in traffic for the month of December as compared with the preceding months. The principal classes of merchandise carried during the year were clothes and furs. Among the imports, the largest item was one of about £307,500 for women's outer clothing brought from France. Fur goods valued at about £78,000 were also carried from France. In the export trade, the different classes of goods dealt with were more evenly represented. One of the chief items were men's and boys' woollen clothing, etc., to the value of £27,700.

THE SECRETARY of the Department of Scientific and Industrial Research makes the following announcement. The Lord President of the Council has established an Inter-Departmental Committee on Patents with the following terms of reference: (1) To consider the methods of dealing with inventions made by workers aided or maintained from public funds, whether such workers be engaged (*a*) as research workers, or (*b*) in some other technical capacity, so as to give a fair reward to the inventor and thus encourage further effort, to secure the utilisation in industry of suitable inventions and to protect the national interest; and (2) to outline a course of procedure in respect of inventions arising out of State-aided or supported work, which shall further these aims and be suitable for adoption by all Government Departments concerned. The Secretary to the Committee is Mr. A. Abbott, to whom all communications should be addressed, at 16 and 18 Old Queen Street, Westminster, London, S.W.1

COTTON IN THE WEST INDIES.—Advices from the Imperial Department of Agriculture for the West Indies, dated December 14, state that the Pink Boll Worm of cotton, *gelechia gossypiella*, has unfortunately appeared in Montserrat and St Kitts. Sir Francis Watts states that it has to be recognised that the appearance of Pink Boll Worm in the West Indies is a serious matter for the Sea Island Cotton Industry, and one of gravity for these islands, and particularly for those which like Montserrat and St. Vincent, depend so largely upon the cultivation of cotton for their means of support. The whole question must engage th

serious attention of all concerned, including the Government and the cotton growers. It is improbable that the present cotton crop will be very materially reduced by the pest; and it is hoped that next year's crop will be safeguarded to a large extent by the steps that will be taken for the control of the pest.

## BOOKS RECEIVED.

"First Course in General Science." By FREDERICK DELOS BARBER, A M., MERTON LEONARD FULLER, A.M., JOHN LOSSEN PRICER, A.M., and HOWARD WILLIAM ADAMS, B.S. 607 Pages Illustrated. London: G. Bell & Sons, Ltd. Price 9s. net.

"Ammonia and the Nitrides, with Special Reference to their Synthesis." By EDWARD B. MAXTED, Ph.D., B.Sc., F.C.S. Illustrated, 112 Pages. London · J. & A. Churchill. Price 7s 6d. net.

"Lectures on the Principle of Symmetry and its Applications in all Natural Sciences." By F. M. JAEGER, Ph.D. Second augmented Edition, with 173 diagrams and three portraits. 347 Pages. Amsterdam: Publishing Company "Elsevier." 1920.

"Principles of Wool Combing." By HOWARD PRIESTMAN. Second Editon, enlarged and revised. 232 Pages. London: Bell & Son. Price 12s. net.

"The Chemistry of Enzyme Actions." By K GEORGE FALK, American Chemical Society Monograph Series. 136 Pages. New York: The Chemical Catalogue Company.

"The Physiology of Protein Metabolism." By E. P. CATHCART, M.D., D.Sc, F.R.S. 176 Pages. London: Longmans Green & Co. Price 12s. 6d net.

## MEETINGS FOR THE WEEK

*Monday, March 21.*

Royal Society of Arts, 8. "X-Rays and their Industrial Applications" by Major G. W. C. Kaye.

*Tuesday, March 22*

Mineralogical Society, 5.30.
Institute of Metals, 7.30. (At Birmingham).
Faraday Society, 8 "Some Aspects of the Scientific Work of the late Lord Rayliegh (Presidential Address)" by Prof. A. W. Porter. "The Forms of Electro-deposited Iron and the Effect of Acid upon its Structure" by W. E Hughes. "The Electrolytic Recovery of Zinc" by S. Field. "Electrolytic Reduction of Glucose" by Prof. A. Findlay and V. H. Williams.

*Wednesday, March 23.*

Conjoint Board, 5.

## NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemical Apparatus, &c., for review or notice to be addressed to the EDITOR.

**SUBSCRIPTIONS,** £1 12s. per annum, payable in advance, should be addressed to the MANAGER.

**BACK NUMBERS and VOLUMES** can be purchased on application to he MANAGER.

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## ADVERTISEMENTS.

THE CHEMICAL NEWS.

VOL. CXXII., No. 3180

# LUMINESCENCE IN INORGANIC BODIES.

(A CRITICAL SURVEY).

By J. FREDERICK CORRIGAN.

It is a commonplace in science that many of the old, long-familiar, and most frequently occurring of the natural phenomena which everywhere beset us, often fall into the category of things unexplained. By some ironical humour of the Gods, the quibbles and uncertainties of scientific knowledge often seem to centre around common occurrences, and to escape altogether the more complicated points. There exists a most wonderful and satisfactory way of accounting for the at one time mysterious deviations of gases from their "laws." The phenomena accompanying the electrolysis of solutions can be explained, and we can even account for the tricky habit which some organic compounds have of behaving as if they possessed two alternative formulæ. But where is the all-comprehensive theory which satisfactorily explains all the numerous facts connected with luminescence? It is not yet formulated. And luminescence is a phenomenon which must have set the human mind wondering ages before even an explanation of the nature of light was considered necessary. Luminescence has long been observed. It occurs both in the organic and in the inorganic kingdoms. Deep-sea creatures depend on it for their light; it is as the love-token in the insect world; and under some circumstances it is even the sign of death and decay.

However, it is beyond the scope of this paper to deal with the numerous forms of organic luminescence, our attention being given solely to the luminescence of the mineral world. Even here, the phenomena is very widespread and diverse, both in its mode of production and in its effects. Until recently, the literature on the subject was scant, contradictory, and unsatisfactory in the extreme. Even the very name of the phenomena has not yet been fully agreed upon, the terms "luminescence" and "phosphorescence" still being arbitrarily employed, although "fluorescence" is used to denote a modification of the phenomenon.

On consideration, it is evident that fluorescence is a form of phosphorescence, and for these two phenomena the term *luminescence* has been proposed by Wiedemann. Wiedemann suggests that all phenomena which involve the evolution of light not due to ignition should be classed under the general terms luminescence. Immediately we have two divisions:—

$$\text{Luminescence}\begin{cases}\text{Fluorescence}\\ \text{Phosphorescence (Photo-luminescence).}\end{cases}$$

When a body, such as a sulphide of an alkaline earth metal is stimulated by light, the later is absorbed, and at the same time, gradually evolved, even after the light stimulation has ceased.

A fluorescent solution, however, only gives off light as long as the light-stimulus is applied. If the source of light is cut off, the fluorescence immediately ceases. This, therefore, would appear to be the chief point of distinction between phosphorescence and fluorescence. Phosphorescence which is caused by light-stimulus may conveniently be named *photo-luminescence*, or the term *phosphorescence* itself may be retained for that particular phenomena.

Photo-luminescent or phosphorescent compounds were known long before they were "discovered" by the medieval alchemists. They were wondered at, and their preparation was very much sought after, but it was not until the close of the last century that a real enquiry into the nature and properties of these substances was begun.

Perfectly pure substances are considered to be incapable of phosphorescence, the phenomenon only being supposed to take place in a solid solution. If the supposition is correct, the amount of impurity required to produce phosphorescence must be exceedingly minute, for in the phosphorescent compounds prepared by H. Jackson (*Phil. Mag.*, 1898, xlvi., 402), the amount of impurity present was too small to be detected by ordinary means. Again, it is considered that a certain proportion of the impurity corresponds to a maximum effect of phosphorescence, the effect being diminished if the amount of the impurity is decreased or increased (Klatt and Lenard, *Wied. Ann.*, 1889, xxxviii., 90).

In confirmation of this, it is interesting to note that Mourelo (*Compt. Rend.*, cxxiv. (22), 1237) prepared pure strontium sulphide by reducing the sulphate with carbon, and also by treating the carbonate, heated to redness, with $H_2S$. The resulting purified product, he found, did not phosphoresce. If heated slightly, so that a little of the sulphide was oxidised to sulphate, the substance exhibited a brilliant phosphorescence. When, however, the substance was strongly heated, so as to convert a larger percentage of sulphide into sulphate, no phosphorescence was apparent, but on subsequent reduction with charcoal, the phosphorescence was again regained.

The nature of the impurity has apparently a great influence upon the colour of the phosphorescence. This may be strikingly demonstrated by placing in test tubes quantities of an alkaline-earth sulphide to which traces of metallic salts have been added. On exposing to the light of a magnesium ribbon, the tubes will be seen to glow in different colours, according to the nature of the impurity present. The following table, constructed mainly on the observation of Mourelo and Becquerel, depicts the variation in colour of the phosphorescent alkaline-earth sulphides, due to the presence of a second substance in minute amounts.

| Impurity. | Colour of Phosphorescence |
|---|---|
| Mn | Yellow |
| Zn | Blue Green |
| Na | Yellow Green |
| Bi | Blue |
| Al | Red |
| Rb | Crimson |
| Li | Green |

(Mourelo, *Compt. Rend.*, cxxvi. (21), 1508; cxxix. (26), 1336; Becquerel, *Compt. Rend.*, cvii., 892).

The temperature at which the phosphorescent substance is maintained has also an influence upon the colour of the resulting phosphorescence

Becquerel found that with a specimen of strontium sulphide, the colour of the phosphorescence could be altered from violet to orange simply by varying the temperature. Thus:—

| Temp. | Colour of Phosphorescence |
|---|---|
| 20° C ... ... ... ... ... ... | Violet |
| 40° C. ... ... ... ... ... ... | Blue |
| 70° C. ... ... ... ... ... ... | Green |
| 100° C. ... ... ... ... ... ... | Yellow |
| 200° C. ... ... ... ... ... ... | Orange |

Another factor which determines the character of the phosphorescence is the intensity of the light-stimulus. J. R. Mourelo (*Compt. Rend.*, 1899 cxxxviii., 557), showed that the phosphorescence of strontium sulphide is more intense and of a longer duration when the sulphide is light-stimulated by diffused light. Light stimulation by bright sunlight shortens the duration of the phosphorescence and lessens its intensity. The sulphides of calcium, barium, and zinc also share this property.

Diffused light also appears to increase the sensibilty of the substance to light-stimulation, and this sensibility may be further increased by repeated exposures to different light. Mourelo developed the sensibility of a specimen of strontium sulphide to such a degree that the light of a candle was sufficient to exert the necessary light-stimulus required for the phosphorescence. One specimen of strontium sulphide, when phosphorescing with sufficient intensity, can excite phosphorescence in another sample of the sulphide, although to a less degree. This phenomenon has been termed "auto-excitement", and it occurs when a flask containing a phosphorescent sulphide is exposed to light. Only the outside layer of the sulphide receives the direct light-stimulus, but it is found that the whole mass is phosphorescent, but in zones of decreasing intensity towards the centre of the flask.

From the above, it would appear that phosphorescence is governed by a variety of conditions. Summarising these it will be seen that the phosphorescence of an alkaline-earth sulphide is dependent on:—

1. The amount of impurity present.
2. The nature of the impurity.
3. The temperature of the phosphorescent substance.
4. The intensity and duration of the light-stimulus.

In the case of fluorescence, it has been shown that the phenomenon is often due to the presence of an impurity. It is really remarkable that the presence of a second substance in minute amount should impart such a striking property to the main substance. A theory which would attempt to satisfactorily explain this must be of a dual nature. It must account for the physical as well as the chemical action of the impurity.

Photo-luminescence is really a case of *light-storage*, or rather the storage of some form of light energy. If it were possible to measure the total amount of light-energy taken in by the phosphorescent substance, and also the total amount of light-energy subsequently evolved as phosphorescence, the two values would doubtless coincide. After all, the storage of energy in its various forms is not a novel idea. Mechanical energy, heat and electricity, can be stored in some potential form; why not also light?

The work of Dewar (*Proc. Roy. Inst.*, 1895, xiv., 115) on phosphorescence at low temperatures also supports this view. Most forms of energy disappear at low temperatures, in addition to being made greater by increase in temperature, and the phenomenon of phosphorescence is no exception to the rule.* Dewar found that the sulphide of the alkaline-earth metals, whose phosphorescence is increased by rise in temperature, ceased to be phosphorescent when cooled to —80° C., but on being returned to ordinary temperatures, their phosphorescence was regained. Although, at these low temperatures, the phosphorescent sulphides are unable to evolve light-energy, they are capable of absorbing it, and of releasing it at higher temperatures. For instance, calcium sulphide, when light-stimulated at a temperature of about —80° C. does not exhibit phosphorescence, but on warming up to ordinary temperatures, the usual phosphorescence is obtained. Thus light-energy, which is absorbed and stored in a potential form at a temperature of —80° C., can be completely evolved at higher temperatures. If the light-stimulation is carried out at still lower temperatures, the intensity of the resulting phosphorescence is increased.

The duration of phosphorescence varies greatly. In some cases it may last for days, whilst in others it is almost instantaneous. Besides being dependent on the duration and intensity of the light-stimulus, the duration of the phosphorescence is to a large extent governed by the intrinsic physical, or chemical properties of the body itself. From time to time, suggestions have been put forward for the construction of an instrument which would measure the duration of the light evolved by a body possessing only a short-lived phosphorescence, but only two have really materialised; they are the phosphoroscopes of Becquerel and Lennard. The former deserves a brief description.

Becquerel's Phosphoroscope consists of a shallow metal drum having two apertures cut in both ends, and exactly opposite each other. Inside the drum and near each end are place two discs which have been divided into sectors, and each alternative sector cut out. The discs are so arranged that when the sector at one end closes the aperture, light is freely admitted at the other end of the drum. Thus it is obvious that when light is admitted by a body placed in the drum, the aperture to which the eye is placed will be closed by one of the sectors, and will only be opened when a sector crosses the aperture at the opposite end of the drum. When the discs are rapidly rotated, the phosphorescent substance inside will be exposed to light and to the eye in rapid succession so as to produce a continuous vision. By this means, knowing the number of sectors and the rate of rotation, it is possible to estimate the duration of the phosphorescence of the experimental substance.

### *Other Types of Luminescence.*

Light is not the only form of energy which can act upon bodies so as to cause them to exhibit luminescence. Luminescence due to other causes has long been known, and the phenomenon admits

*Dewar observed that many non-phosphorescent bodies, such as ivory, rubber, cotton-wool, paper, gelatine, etc., become phosphorescent at the temperature of liquid air. This apparent contradiction deserves investigation.

of certain more or less arbitrary divisions. Thus we can distinguish several classes of luminescence which are usually named according to their exciting cause. They are:—

1. Tribo-luminescence ("Luminosity by Attrition").
2. Thermo-luminescence.
3. Chemi-luminescence.
4. Crystalo-luminescence.
5. Electro-luminescence.

These subdivisions of luminescent phenomena, together with photo-luminescence (phosphorescence), and fluorescence, are all included in the generic term *Luminescence* (Wiedeman). As their cause is probably fundamentally the same, it will be desirable to deal with each class in turn.

*Tribo-luminescence.* — Thomas Wedgwood is generally considered to be the discoverer of "Luminosity by Attrition," although it was observed some years before by Du Fay (1735). In a paper on "The Production of Light from Different Bodies by Heat and Attrition" (*Phil. Trans.*, 1792, 17, cxxviii., 215), Wedgwood put forward the view that almost all substances possessed some latent "phosphorism" which might be made apparent by heat or by attrition (rubbing). His experiments extended over a wide range of minerals obtained from different localities, and even to this day his paper has not been surpassed for painstaking care and thoroughness by any other workers on the subject.

Wedgwood observed that the colour of the light varies according to the minerals used. He also noticed that the "bodies give out their light the instant they are rubbed on each other, and cease to be luminous when the attrition is discontinued." He paid attention to the "fœtid smell" which invariably accompanies the phenomenon of tribo-luminescence, although he offered no explanation of the peculiar odour. The cause and nature of this odour is still unknown. Quartz exhibits tribo-luminescence even under water, alcohol, or ether. This fact has prompted a writer in *Nature* (Nov. 4, 1920) to suggest that the apparently volatile odoriferous matter could probably be obtained in solution by grinding quartz under a suitable liquid. However, at present, speculation is of little use until more experimental evidence has been accumulated, for with regard to the latter, our knowledge of the subject is little more than it was in Wedgwood's time

*Thermo-luminescence*, as its name implies, is the phenomenon which accompanies the heating of of certain substances to temperature below red heat. Wedgwood carried out experiments on thermo-luminescence by dropping substances on to a heated iron plate. He found them to emit "considerable light." Many bodies emit light when heated. In the case of chlorophane, a variety of fluorspar, the heat of the hand is sufficient to cause the mineral to luminesce vividly.

But here again our knowledge of the subject is almost zero. Ordinary phosporescence or photo-luminescence might very well be considered to come under the heading of thermo-luminescence, for below a certain temperature no amount of light-stimulation will cause luminescence, but on warming up to ordinary temperatures, the luminescence becomes apparent. One might postulate and determine a critical temperature of luminescence, and thus absorb the category of thermo-luminescent bodies into the larger photo-luminescent classification. Wedgwood noticed the fact that the luminescence decreased with subsequent heating, although after many periods of heating he was never able to *drive* the luminescence off, as it were. However, modern investigation would probably be able to determine whether repeated periods of heating are able to rid a body of its luminescence, and whether after light-stimulus at ordinary temperatures, the body again becomes luminescent on heating. This piece of simple experimental evidence would enable us to definitely fix our views with regard to photo and thermo-luminescence, and most probably the two divisions would become absorbed in one larger category.

*Chemi-luminescence* includes all cases of chemical action which give rise to luminescence without any apparent rise in temperature. The luminescent properties of phosphorous in contact with air and moisture are well known and have been carefully studied. The luminescence of decaying vegetable matter, due to the presence of luminous fungi and bacteria, have also rather prematurely been classed under this heading.

*Crystalo-luminescence.*—Certain salts, on crystallising from suitable solvents, give out a luminescence of short duration at the moment of crystallisation. The luminescence of arsenious acid crystallising from HCl has long been known. Berzelius noticed that saturated solution of sodium fluoxide evolved a momentary yellow-light when crystallising.

Bandrowski (CHEMICAL NEWS, 1894, lxx., 313) studied the luminous phenomena attending the crystallisation of NaCl, KCl, KBr, $K_2SO_4$, $KNO_3$ from aqueous solutions. He also observed a luminescence which occurred when salts were precipitated from the aqueous solutions by means of HCl. Sodium chloride, he states, gives a striking result, the light evolved being of a greenish-blue colour, and of considerable intensity. Bandrowski considers that luminescence is brought about by the union of oppositely-charged ions from the solution. This statement he regards as confirmed by the fact that only salts which are electrolytically dissociated exhibit the phenomenon.

Farnau (*J. Phys. Chem.*, 1913, xvii., 637) has investigated the crystalo-luminescence of the haloids of Na, K, Cd, Zn, Hg, Li, Rb, and Cs. He extends his observations to luminescence of all kinds, which he considers to be due to obscure chemical actions. If the rate of the reaction is increased by means of catalytic agencies, or by temperature, the intensity of the luminescence is increased in proportion. According to Farnau, the nature of the luminescence depends only on the metallic content of the compound, and is the same howsoever produced.

*Electro-luminescence.*—The circumstances under which bodies can be made luminescent by electrical means are well known, and it is in this branch of the study that most of the work connected with luminescence has been performed. Many substances, especially diamonds and rubies, become luminescent more or less readily when subjected to the action of cathode rays, X-rays, radium emanation, ultra-violet light, and other forms of radiant energy. Rarified gases also become luminescent when subjected to the action of

the cathode rays. These appear to be the only known conditions under which gases become luminescent, although Newall (*Nature*, 1897, lvi.) has apparently observed luminescent phenomena attending the compression of a gas from low pressures up to ordinary pressure.

Obviously, the phenomenon of luminescence in rarified gases is due to the operation of some kind of radiant energy, and Jackson (*Trans. Chem. Soc.*, 1894, cxxxiv.) put forward the suggestion that the colour of the sky might in reality be of a luminescent nature, the highly rarified gases existing on the fringe of the earth's atmosphere becoming luminescent under the influence of the solar radiant energy.

Such are the main departments into which all luminescent phenomena are divided. Although luminescence is the study in question, we for the most part still grope in darkness when considering it In every branch of the study the possibilities of research are enormous, and long vistas of the unknown await the scientific man who undertakes a close and persistent investigation.

But our article would be incomplete without a short reference to the

*Theories of Luminescence.*

Under this heading we shall confine ourselves to a rapid survey of the theories of photo-luminescence (phosphorescence) only. As they are very numerous, and as each investigator appears to have his own particular theory, it will be convenient here to gather them up into classes or types, for each theory conforms more or less to a standard type.

*Actual Absorption of a Material Light.*—All early theories are based on this conception, and only differ in the explanation of the nature of the light emitted (Boyle, Canton, &c.).

*Theories Involving Ionic Changes.* — These theories which attempt to explain the apparently necessary presence of minute traces of impurities in phosphorescent substances, regard the phosphorescent body (alkaline-earth sulphide) as containing in solid solution a heavy-metal sulphide. By the act of solution the latter substance is decomposed into ions, which are further split up by light into electron-like particles. When these latter unite to re-form ions, light is emitted, and thus a phosphorescent state is set up (De Visser, *Chem. Centr.*, 1902, i, x., 583; Belby, *Nature*, vol. 1904-5).

*Theories Involving Chemical Changes.*—This type of theory may be stated as follows: When a substance A becomes luminescent under the influence of light, it is converted into a new substance B. This latter is destroyed by heat, being converted back again into A. Thus luminescence is the energy which is evolved as a result of the transformations of the substances A and B. When thermo-luminescence does not occur, the compound B is probably of an unstable nature, and is decomposed at the instant of its formation.

By this theory, the persistence of phosphorescence after the light-stimulus has passed may be regarded as thermo-luminescence at ordinary temperatures (A. Debierne, *Compt. Rend.*, 1906, cxliii.; Wiedmann and Schmidt, *Ann. der Physik*, 1895, lvi., 246; Nichols and Merritt, *Phys. Rev.*, 1908, xxvii., 367; Voigt, &c.).

*Electron Theories.*—In these theories it is supposed that under the influence of light, electrons are emitted from the phosphorescent body. The electrons, however, are only evolved from certain "centres," and not uniformly from the whole area of the alkaline-earth sulphide exposed to light. The areas or localities from which the electrons have been liberated now acquire a positive charge of electricity, whilst the electrons themselves become attached to the sulphur atoms. It is in the return of the electrons from the sulphur atoms to their original "centres," and in the subsequent neutralisation of charges that the phenomena of phosphoresana has its rise (Lennard, *Ann. der Physik*, 1910, xxxi., 675; Stark, *Prinzipien der Atomdynamik*, 1911; Allen, "Photo-Electricity," 1913).

Although most of the theories may be referred to the above types, the list is by no means exhausted. However, space doos not admit of any one of them being treated in detail. The most rational and far-reaching explanation of phosphorescence will probably be based on the belief held towards the end of the last century, that in some manner, light or some accompanying-light energy is held by the substance in the form of a *strain* of energy, and that during a recovery from the strain, light is emitted, in much the same way as energy can be stored in the form of a strain, by twisted elastic cords. Klatt and Lennard added substance to this view by showing that the alkaline-earth sulphide entirely lose their property of phosphorescence when subjected to high pressures.

But here we must leave the subject as it stands. A complete understanding of the phenomena involves a knowledge of the play and interplay of atomic forces; a knowledge of which is yet lacking, but towards which the physicist is slowly but surely groping his way. Meanwhile, much remains to be done in revising and placing on a firm scientific basis many observations, the accuracy of which is to be doubted. The varied phenomena of luminescence should cease to be regarded as scientific curiosities, but should more properly be looked upon as manifestations of some unknown natural law.

## SOME TECHNICAL APPLICATIONS OF SPECTROSCOPY DURING THE WAR.

By A. de GRAMONT.

Some years ago, the author showed that the spark discharge of an electrostatic condenser when it illuminates the surface of a solid or fused compound gives a complex spectrum in which *all* the constituent elements of the compounds exhibit their individual line spectra. The spectrum thus produced may be considered to be obtained by the super-position of the spectra of the compounds, in which, of course, the stronger rays of one element may eclipse the fainter lines of another element in their immediate neighbourhood. The spectra of compounds thus give time dissociation spectra in which all the substances present can be recognised, the sensibilities being different according to the element under consideration The apparatus used by the author consisted either of a spectrograph with two crown glass "uviol" prisms, or one with a single quartz prism, the former giving the best results. When the substance under examination consisted of a non-conducting

material, such as a precipitate or powder or earthy mineral, a suspension of it in a fused alkaline salt was made. Certain rays which the author called "ultimate rays" were found to be always the last to disappear as the amount of the element was diminished. These rays are not necessarily the strongest or brightest in the spark spectrum; they are found in the arc spectrum and in the spectra of very hot flames, such as the oxy-hydrogen or oxy-acetylene flame. Certain metalloids, such as chlorine, bromine, iodine, oxygen, sulphur, selenium, and nitrogen, do not give arc spectra nor ultimate rays, while others, such as boron, carbon, silicon, phosphoric, arsenic, tellurium, exhibit these rays, and although their detection by spectrocopy is not easier than by modern analytical methods, it is very usefully employed in the case of the co-existence in a compound of several elements. The ultimate rays of these metalloids are situated in the very refrangible part of the ultra-violet.

The author applied this method of investigation to many metallic products, and drew interesting conclusions as to their purity. He found that some specimens of German steels, for example, gave extremely complex spectra, showing the presence as essential constituents of chromium, nickel, vanadium, and tungsten. Minute traces of boron in a vanadium steel make it extraordinarily hard. So-called pure specimens of copper always contained iron and carbon, and often calcium and silver. Commercial platinum contained copper, silver, and gold, as well as iridium, rhodium, and palladium, while zinc always contained traces of cadmium, lead, and iron. An interesting discovery made by the help of this method was the fact that the ash of tissues and various physiological products always contains zinc, and it has been established that zinc is a normal constituent of all animal cells.—*Bulletin Officiel de la Direction des Récherches Scièntifiques et Industrielles et des Inventions,* July, 1920.

## A CRITICAL STUDY OF FERTILISER EXPERIMENTS.

By C. B. LIPMAN and G. A. LINHART.

AMONG the most expensive and time-consuming experiments in agricultural investigations have been those which attempt to ascertain the proper chemical amendments or fertilisers for soils. This applies in particular to the long-term fertiliser experiments like those at Rothamsted in England, at State College in Pennsylvania, and at Wooster and Strongsville in Ohio. Conceived and inaugurated, as they were, at times when little or no real authentic information was available relative to the nature of soils and plants, it is but natural that fallacious and short-sighted planning should have dominated them. It occurred to one of us that as critical thinking in this field has become more general, and facts more plentiful, it is high time that fertiliser experiments in general and the "long-term" experiments in particular be subjected to critical scrutiny. It seemed desirable to employ the statistical method for this purpose, particularly in view of the striking results obtained in this laboratory by our former associate, D. D. Waynick. It seemed clear to one of us that if, as Waynick, and Waynick and Sharp had demonstrated, the variability of soils and of plants is very large even within selected and presumably uniform material, one could not expect previous fertiliser experiments to be of much value, since the factor of variability has been entirely ignored in their arrangement and study, and the probable error to which they were subject was not determined. Accordingly, Lipman and Waynick began in January, 1919, a systematic study by statistical methods of the results of fertiliser experiments at the Ohio and at the Pennsylvania Agricultural Experiment Stations. Mr. Waynick left this laboratory the following July, but with a number of interruptions, the work has been continued, and we hope to issue the voluminous data, together with a critical discussion of them, in due course. Since the work may be a long time in the press, we deem it wise to present here a few of the salient and most important findings of our studies, so that our colleagues may be apprised of what we consider to be an investigation of a fundamental nature, not merely on account of the importance of the subject itself, but because of its important bearings on agricultural research.

It seems that the originators of both the Ohio and the Pennsylvania experiments saw the value of replicating check plots, while not recognising the value of such replication for the treated plots. Only in the case of two complete fertiliser plots in the Ohio experiments, was the fertiliser treatment the same. In all the others every treatment was different from that of every other. This situation renders it difficult to subject their data to statistical treatment in the most desirable way. Fortunately, however, the long series of years during which the plots were studied gives, in a certain sense, a replication of plots of each kind. Our procedure has been, therefore, to group the plots in different ways, including the following :—

1. All the check plots for each year.
2. One check plot for all the years.
3. All the plots treated with "one-element" fertilisers in one year.
4. Every "one-element" fertiliser plot for all the years.
5. The same double study for the "two-element fertiliser plots."
6. The same for the "three-element" fertiliser plots.

In addition to these groupings, others were made in which a given plot was studied with each crop in the rotation, so as to allow of only three to eight "yield" data for each plot. It may be said in passing that the rotation study included in these experiments only serves to complicate a situation which was already sufficiently difficult. We shall show in detail in the complete study which is to be published, that these experiments are utterly inadequate for solution of the questions involved, and that all such fertiliser experiments are so fallacious as that they do not justify the use of the large amounts of money that are constantly being lavished upon them.

For the sake of brevity, only a few of our findings, from the study of the Ohio data alone, are summarised here.

1. The "one-element" fertiliser treatments show no significant increases in yield over the yields

obtained on the untreated check plots. All statements to the contrary which have heretofore been made are erroneous, and the data on which they are based were obtained by a misleading method of procedure and evaluation.

2. The "two-element" fertiliser plots give definite increases in yield over the untreated control plots. Whether or not the increases are profit-yielding, however, is a question which will be discussed later.

3. The "three-element" fertiliser plots give definite increases in yield over both the untreated control plots and the "two-element" fertiliser plots. Here again, the question whether the increases are profit-yielding still remains to be determined.

4. The kind of fertiliser used seems to have been without significance, one being just as good as another, subject to the limitations above noted.

5. The amount of fertiliser used seems likewise to have been without significance (subject to the same limitations).

6. Even when fertiliser experiments are properly planned, and the results adequately studied by statistical methods, our present knowledge of the enormous variability of all soils and plants renders the data from any given fertiliser plot of value only on that plot, no matter how near the experimental one. This important consideration renders it highly probable that no fertiliser experiment as ordinarily conducted is possessed of sufficient practical value to justify the large expenditure of money, time, and energy involved.

We wish to emphasise that we are not desirous of making a fetish of the application of statistical study to fertiliser experiments. Nevertheless, we must say that if statistical methods, inadequate as they may be, should not prove applicable to an evaluation of the results of fertiliser experiments, the latter must be accounted of even less value and significance than we have here accorded to them.—*Proceedings of the National Academy of Sciences of U.S.A.*, November, 1920.

## ELDRIN, A NEW PLANT CONSTITUENT.*

By JOHN URI LLOYD, Ph.M.

For thirty or forty years in the experiments I have made with drugs, plants, and plant structures, I have met continuously the fact that linked with each plant texture there was something present that under the influnce of an alkali gave a yellow colour. For example, strip a paw-paw of its bark and touch the white inner surface with a solution of potash—now it turns yellow. There is probably one rule in this as elsewhere, and that is the rule of exceptions. I hope to find one white blossom that will not turn yellow. If I do, the exception may be of help to the botanist, for it may be the forerunner of a class distinction.

For years this yellow phenomenon was before me, but I could not catch the material that produced it. About a year-and-a-half ago I decided that if I isolated this yellow something that pervaded all plant tissues so linked with imprities as seemingly to defy isolation, it must be obtained from something that is white, something that does not carry a mass of extraneous material to contaminate the principle desired. Then it occurred, why not use the petals of a *white* flower to get this *yellow* something?

The elder was then in bloom. These, I found, turned deep yellow with ammonia gas. I procured 50lb. of elder flowers, put them in a percolator, made a tincture, and worked it by means of neutral solvents and excluders, to rid the product of the alcohol, chlorophyl and wax. I had 5 gallons of the chlorophyl-free liquid, and said to Mr. Miller, who was assisting me: "Place the jar in a cold situation, and to-morrow morning I shall examine it." Next morning I tipped the jar very carefully, and all down the sides were little white concretions about the size of pin heads. It was the thing I have been seeking forty years.

I took one of those pin heads to the laboratory and dropped it into distilled water and it did not dissolve. I added ammonia—behold! it immediately dissolved, the liquid turning deep yellow. It was only the size of a pin head, but there were thousands of them. An they kept increasing in size. The marvellous phase of this subject is, I got 11oz. (crude) of that substance out of that 50lb. of elder flowers. Before that, by reason of faulty research, I could not get a grain from anything.

The first thought of a pharmacist is, what value a new substance may have in medicine. Alas, the greater part of my work has been the repeated finding of something that had no value. I sent some of this material to Prof. R. Adams Dutcher, University of Minnesota, requesting that he make a physiological examination of it. His preliminary report was to the effect that, according to a preliminary investigation, it had no physiological action. May I not ask, should a peculiarity of action be expected of a substance pervading plant tissues everywhere. (I had vitamics in mind, there was reason to hope that a general life supporter of plant life, serviceable to animals, could be found and isolated. Not a poison of energetic action. This, I accept, Dr. Dutcher demonstrated as a fallacy in the direction of this substance).

In this cylinder I have distilled water, and I propose to put into the water a small amount of this material. Note that it settles to the bottom. It is perfectly insoluble. One grain shaken with a gallon of water apparently disappears, but if let stand until the next day, behold, it is all at the bottom. I now shake the mixture, and pour half of it into another cylinder, then add a little ammonia water—note the change in colour, to deep yellow. A very delicate reagent is it for an alkali. Let us now make both liquids yellow. Into one I pour diluted sulphuric acid, in excess, to destroy the ammonia. The liquid becomes colourless.

Now the question came to me, "Why is the white flower white when it has the yellow material in it in such quantity?" Then I figured to myself it must be because the white petals carry also an acid which in contact with the yellow material makes it white. In other words, would the white flower be yellow if there was an alkali in the petal instead of an acid? Crushing the flower in a mortar with a little distilled water gave a sharp acid reaction. Blue litmus turned red at once. The acid was present.

*Portion of an address on Plant Constituents delivered at the Ohio State Eclectic Medical Assoc. From the *Eclectic Medical Journal*, Dec., 1920.

The question arises: What is the use of this thing in nature? I think I comprehend the subject, but it is too great to try to bring before you to-day.

I am going to ask you to be charitable in what I have said concerning the theories I now hold. I may be right and I may be wrong. We can see this colour change and we know that the petals hold organic acid. What of it? I don't claim that anything I have brought is new; quite the contrary. So far as I know, this experiment has not been made. In some literature unknown to me it may be explained. It doesn't matter whether it is new or old—it is a phase in plant economy that is a fact, and may be of service other than as a medicine.

I asked myself: Why the material could not be used to make a test paper? Why would not paper saturated with a solution of this material turn yellow with alkali and colourless with acid? I tried it and it worked. There is a shade between red and blue litmus which makes it difficult sometimes to quite determine the end-reaction. There is no intermediate shade with this.

For example, let us now pour into these tumblers some water, and into the one put some ammonia and in the other dilute sulphuric acid. The paper I hold in my hand has been saturated with a weak solution of this material and dried. I dip it into the acid. See, it is colourless. Now I dip it into the ammonia; it instantly turns yellow.

You ask the name of this material. I call it *Eldrin.* But it may have been long known elsewhere and recorded under a different name or different terms.

## AN EPOCH-MAKING DISCOVERY.

By CHARLES. H LAWALL, PH.M.

IT is bromidic to quote the oft-repeated proverb about the prophet and his own country, and yet none other is applicable to the situation in which Einstein finds himself in Germany while much of the remaining scientific world is doing him homage and dscussing his work on "The Special and General Theory of Relativity."

This is an age of pragmatism, and while the educational attainments of the average individual are higher than ever before in the world's history, it is to be doubted whether there is much sympathy with, or consideration of, abstract principles as a rule, except among mathematicians and physicists.

From the earliest times there have been those who went out of their way to grapple with the unknown, whether or not the rewards were apparent. Babylonian arithmeticians and Egyptian geometers had exercised their mathematical abilities chiefly along the lines of mensuration, with some attention to astronomy, but when the speculators of Hellenic origin appeared, abstract mathematics became a cult which lasted for several centuries, and which influenced human though for all time. Thales, Pythagoras, Plato, Euclid, Aristotle, and Ptolemy, were little concerned with the practical applications of their theories, yet they paved the way for Copernicus, Descartes, Galileo, and Newton, who came many centuries later.

The pupil of Euclid who asked "What do I get for learning these things?" typified a state of mind common to all ages, and probably approaching its highest peak in our own time, as indicated by the general apathy with regard to the underpaid members of the teaching profession, and the attitude of the average school pupil or college student who aims not at perfection in his work but sets his goal at the minimum passing grade.

In Francis Bacon's classification of human knowledge (1630) speculative philosophy occupied a larger proportion of the diagrammatic scheme than would be accorded it by one who attempted a similar outline to-day, and yet the worker in pure research, or the one who discovers and records an abstract scientific principle, may be conferring upon future generations blessings incalculable.

The continuity of scientific effort in any single direction is more evident in our era than at any previous time in the world's history.

More than two thousand years elapsed between the crude steam appliances of Ctesibus and Hero, and the steam engine of James Watt, and outside of one experiment of Leonardo de Vinci, most of the developmental work occurred in the century in which Watt himself lived.

It took comparatively few years for the discovery of the Hertzian waves to find their practical application by Marconi, and yet Hertz and his co-workers never dreamed of such a thing as wireless telegraphy, nor profited by their work except in reputation.

The work of Albert Einstein, which deals particularly with space and time, and which concerns itself in reality with a method of interpretation of old rather than the promulgation of new principles, is looked upon as epoch-making in its possibilities by some of the mathematicians, physicsts, and philosophers, who are in close enough touch with the subject to be able to judge thereof intelligently.

For the individual not actively engaged in the fields of work most directly affected by Einstein's observations, articles have appeared; lectures have been delivered and books have been written for the purpose of stopping down the high voltage of the original communication to a lower potential which will not burn out the mental coils and fuses of the average intellect. Dr. Leffmann has humorously and approximately correctly translated the Einstein idea into the epigrammatic form that: "You cannot tell where you are unless you know what time it is and you cannot tell what time it is unless you know where you are."

In Euclidean geometry, as taught in our elementary schools, descriptions of events in space presuppose the existence of a rigid or invariable body to which such events may be referred.

No cognizance is taken of differences of values in observation, due to the fact that one observer is in motion while the other is at rest, nor of differences in interpretation due to time discrepancies.

In physical science data have long been accumulating for which no use could be found in the calculations of three dimensional or ordinary space. By the introduction of the time factor a four dimensional space-time combination becomes possible, and these hitherto unused data are said to find a place.

In the Einstein method of interpreting mathematical and physical data, the length of a

measuring unit or of the duration of an event are not absolute quantities, as has always been hitherto assumed in physics, but it is declared that they actually have different values for different systems of reference moving with relation to one another.

Newton had established concepts of what it has been customary to call "Absolute true and mathematical time" and "absolute space."

Experiments of certain physicists had proved man's inability to detect absolute motion (motion with respect to the hypothetical æther). This has recently led to the development of a theorem to the effect that "all laws of physical nature should have been formulated with reference to a definite coördinate system, are valid, in precisely the same form when referred to another coördinate system which is in uniform rectilinear motion with respect to the first."

This empirical law is Einstein's "Special Theory of Relativity."

It is a simple matter to make time duration calculations with a clock situated where the event is taking place. It is more difficult to make such calculations with events happening at two different places, for then some elaborate precautions must be taken to bring the two clocks into synchronous agreement. When we come to deal with calculations where the clocks are not at rest with reference to each other, as for instance, when one is on a railway train travelling at a high rate of speed, all ordinary methods of measurement and comparison fail.

Such refinements of observation seem to be beyond our conceptions of practicality, and yet we are assured of their value by those who deal with calculations involving the physical laws, particularly with reference to light.

One of the modern concepts, which is at variance with Newtonian principles, is the declaration that a gravitational field has an influence upon a ray of light. Einstein asserted his ability to prove this by the application of his method to observations and calculations of certain astronomical phenomena. This assertion is said to have been confirmed by observations of the photographic registrations of stars during the eclipse of the sun in May, 1919, and afford justification for the hope that some of the obscure laws of nature may be fathomed by a further pursuit of this subject by those philosophers who are equipped for this recondite branch of human study.

In the words of one of the recent interpreters of Einstein to the multitude this thought is expressed as follows: "The main philosophic achievement of the special theory of relativity is probably the recognition that the description of the event, which is admittedly only perfect, if both the space and time coördinates are specified, will vary according to the relative motion of the observer; that it is impossible to say, for instance, whether the interval separating two events is so many centimetres and so many seconds, but that this interval may be split up into length and time in different ways, which depend upon the observer who is describing it" ("Space and Time in Contemporary Physics," by Moritz Schlick).

The "general theory of relativity" concerns itself with the broader fields of human speculation and endeavour. This is much more daring and less easily comprehended without a knowledge of higher mathematics and there are those among the physicists and mathematicians who characterise it as "Metaphysical Mathematics," and "Intellectual Moonshine."

The fundamental question, "are space and time real?" cannot be answered simply and categorically. Space and time for human comprehension and appreciation are dependent upon the existence of things which lie closer to our senses.

If there were not material bodies we could have no conception of "space", and if no events or changes took place "time" would be devoid of meaning. The world-old question as to what constitutes reality finds the answer of the modern physicist eminently satisfying. "Whatever can be measured is real."

Are space and time real? Both being measurable we unhesitatingly reply in the affirmative. Yet if we perform the imaginary experiment of the celebrated French mathmatician Poincaré, and "suppose that all material bodies should increase over night one hundred fold," we should be unable to perceive the change, for all of our measurement standards and units would have changed likewise. We should still call an inch by that name although it had increased to more than eight feet. How can we argue convincingly about the reality of space, therefore, except as a relative concept.

So in the same way our time determinations become closely associated with physical bodies as our ideas of space, and quantitative determinations are predicated upon some pre-arranged method of synchronising our clocks; otherwise conceptions of simultaneity and equal duration can have no definite and invariable meaning.

The influence of the gravitational field prevents the application of the special theory of relativity to any but systems at rest or moving uniformly and rectilinearly.

The mathematical development of the theory pre-supposes the introduction of the time factor as a fourth coördinate and calling the new and complex curve thus produced the *World-line* of a given point. The final formulation of the Einstein Law is expressed as follows. "The world-line of a material point is a geodetic line in the space continum." The time factor is not introduced simply as such, but as $ct = x_4$ in which $c$ denotes the velocity of light.

The statement that every motion is relative may be looked upon as another way of expressing the view that space and time have no physical objectivity. Space and time are not measurable in the abstract. They constitute the framework which we fill up with physical events, both spatial and chronological.

We gain our knowledge of both space and time by direct experience, so in our everyday life we shall continue to deal with them as heretofore. To the physicist and astronomer, however, new fields of research are already opening, and it is not too much to expect the future to bring us into closer harmony and a more nearly correct understanding of electro-dynamics and gravitational law with a realisation, perhaps, that matter after all is but one of the manifestations of energy.

One comfort for the average student of mathematics is found in the assertion that "Euclidean geometry is to remain valid for infinitely small portions" which includes those within the ken of our ordinary daily life. The trouble with the

whole subject at present lies in the fact that Einstein enthusiasts are presuming to "prove the unprovable", and to make assertions to the effect that there is such a thing as "finite space without boundaries."

Students of philosophy who remember the speculations of Kant in his "Subjectivity of Time and Space," and Locke in his "Essay on Human Understanding," and Leibnitz, the originator of differential calculus, will enjoy the spiritual exhilaration of cleaning out the cobwebs of the mental attic, by reading one of the works which have recently been published in which the subject is discussed with a minimum of complex mathematical details, although it will be realised that workers in physics are rapidly ascending to heights in which the rarefaction of the mental atmosphere will soon make it impossible for the person of ordinary education to accompany them, and in which they will be invisible to those below the cloud strata of higher mathematical formulas.—*American Journal of Pharmacy*, January, 1921.

## PROCEEDINGS OF SOCIETIES.

### THE OPTICAL SOCIETY.

At a meeting of the Optical Society, held at the Imperial College on March 10, Prof. H. F. Newall, F.R.S., gave a lecture on "The Story of a New Star". Available data relating to the known history of several novæ were reviewed, and the interpretation of these discussed, with a view to the formulation of a theory on stellar evolution.

Mr. T. F. Connolly, M.Sc., described and exhibited "A Handy Form of Measuring Microscope." The instrument uses a microscope system of relatively low power. A double image prism traverses the object space, and is controlled by the rotation of a milled band operating a spiral slot. Exit pupil discs of telescopes or other optical instruments and Brinell impressions can be measured by a single contact setting of the edges of the duplicated discs. The range in the experimental instrument is from 1 to 6 mm., and the accuracy when used with a fixed focus for Brinell impressions is about $\pm$ ·02 mm. The reading scale is very open, and is divided to one-tenth mm. No vernier is used.

## NOTES.

The Sir John Cass Technical Institute.—The Fourth Annual Dinner of the Department of Metallurgy was held at the Florence Restaurant, Rupert Street, Piccadilly, on Saturday, March 12. George Patchin, Esq., A.R.S.M., M.I.M.M., Head of the Department, was in the Chair, and the company of more than 100 included present and past students of the Department, the staff, and a number of distinguished guests. Among the latter were Prof. Merrett, of the Royal School of Mines, Richard Davies, Esq., C.B.E., and J. G. Howell, Esq., of the Governing Body of the Institute, and Dr. Charles Keane, Principal of the Institution. The most important event of the evening was a presentation to C. O. Bannister, Esq., A.R.S.M., F.I.C., who, after 18 years' work at the Institute, has been appointed First Professor of Metallurgy at the University of Liverpool. This was in the form of a silver coffee service, designed by Mr. Harold Stabler, and executed by Mr. W. E. Stocker, of the Art Department of the Institute. Prof. Merrett, in proposing the toast of the department, referred to the continued development of the Department since the war, as shown by the increase both in the number of courses, and in the number of students, the latter numbering 138 in the Session 1919-20. He suggested the addition of a course on ore dressing would give greater completion to an already comprehensive curriculum.

British Industries Fair.—While it is impossible at the present stage to give any estimate of the total business resulting from the British Industries Fair at the White City, certain general conclusions may be drawn from the information at present available. Considering the severe and universal nature of the present trade depression, the bookings in most sections of the Fair may be regarded as satisfactory. The results are, however, difficult to give in any concrete form since no one section has enjoyed uniformly large orders, nor any other suffered from uniform lack of orders. It is noticeable that there are many cases of individual firms doing exceptionally heavy business, but throughout the Fair as a whole, business was considerably below that of last year. When, however, the widely different conditions of trade are considered, this fall in orders booked does not mean so great a drop in the actual business transacted, since last year the buyer was giving orders much in excess of his requirements in the hope of securing those requirements from a short stocked supply, whereas this year any orders booked are definite and final contracts. The attendance at the Fair was also highly satisfactory, nearly 65,000 people visiting the White City. Overseas buyers came from fifty different countries, from Chile and China, from Sweden and Singapore. While the bulk of the foreign buyers came from Europe, Holland, Switzerland, Belgium, and Scandinavia being specially well represented, the attendance from the Dominions was also considerable, and many American visitors were seen at the White City. One unexpected feature of the Fair was that, while the luxury trades could not have been expected to enjoy large orders under present conditions, yet many firms producing the highest grade articles received very considerable orders, in some cases even exceeding last year's. The general organisation of the Fair proved satisfactory, and many spontaneous tributes to its smooth working were given by both visitors and exhibitors.

*Birmingham and Glasgow Sections.*—It is understood that the general results of the Birmingham section were well up to expectations, and Glasgow is reported to be doing well, particularly in certain lines of textiles. The visit of H.R.H. the Prince of Wales to the latter section on Tuesday was greatly appreciated by the exhibitors, and helped immensely to stimulate interest in the Fair.

*Foreign Missions.*—The visit of the Foreign Commercial Missions as guests of the Government has been an unqualified success. During their

tour of the three Fair centres and their reception at Manchester, the delegates have enjoyed every facility for a rapid and thorough survey of British industry. The fresh connections formed by the members of the Missions with the leading representatives of the trades of this country should be productive of much fresh business and increasingly harmonious commercial relations between the United Kingdom and the Continent.—*Board of Trade Journal*, March 10.

Diamond-Cutting School in South Africa.—According to the local press, a school for training men and women in diamond cutting is shortly to be established, probably in Johannesburg. The Transvaal Provincial Council has voted £15,000 for the purpose, which will provide for suitable premises and machinery, a highly-skilled technical head, and competent assistants. In the opinion of a member of the Provincial Council, the school should be completed by about the end of April. One of the drawbacks to the establishment of a diamond-cutting industry in South Africa in the past has been the alleged absence of cutters, but with the establishment of this school, which will teach the work thoroughly and completely in all its branches, there should be nothing to prevent the building up of a large and flourishing industry.

State-Owned Arsenic in Queensland.—Among the trading enterprises of the Queensland Government is an arsenic mine, from which about 3,000 tons of ore have so far been obtained at a gross expenditure of some £17,000. The ore is passed on to arsenic treatment works, also owned by the State, whose aim is to afford relief from the very high prices ruling for arsenical products. During the last financial year, the gross expenditure on the works was £14,040, bringing up the total since the commencement to £23,311. The arsenic produced is distributed among the farmers of the State at £10 a ton for the destruction of prickly pear, and at £23 a ton for cattle dips and other farm requirements.

Dyestuffs (Import Regulation) Act, 1920.—The list of products covered by the Dyestuffs (Import Regulation) Act, which has been drawn up in consultation with the Dyestuffs Advisory Licensing Committee, is now available, and may be obtained on application either to the Board of Trade, Industries and Manufactures Department, Great George Street, Westminster, London, S.W.1, or to the Dyestuffs Advisory Licensing Committee, Board of Trade, Danlee Buildings, 53, Spring Gardens, Manchester.

Contribution to Study of the Mechanism of the Fertilising Action of Sulphur.—A certain number of researches have demonstrated that flowers of sulphur, applied to the soil in suitable quantities, act as a fertiliser and increase yields. One of the essential elements in plant life, sulphur exerts at least a double action. In the first place it supplies sulphuric acid, by bacterial oxidation in the soil, directly assimilable, presence of which especially in non-calcareous soils, permits absorption of certain mineral elements (potash, iron oxide, alumina, and even manganese). Then it facilitates the work of ammonia bacteria and nitrifying bacteria, thus placing larger quantities of nitrogen at the disposal of the plants. Such are the facts acquired by experiment. It has even been thought that sulphur favours development of nodosities in the roots of leguminous plants Experiments made in Algiers in 1918 and in the Jardin des Plantes of Nancy in 1920 to elucidate this question, with peas, haricots, *Lathyrus Ochrus* and *Lupinus Albus*, grown in pots containing sulphurised soil in the proportion of 100, 200, 300 kilogrms. of sulphur per hectare gave no clear results, perhaps because the sub-soil of mould was rich in nitrogen. These experiments demonstrate, once more, the fertilising action of sulphur as illustrated by the following figures for the haricot Souvenir de Dreuil:—

| | Number of Seeds. | Weight. Seeds. grms. | Weight. One Seed grm. |
|---|---|---|---|
| Without sulphur ... | 13 | 4·9 | 0·376 |
| 100 kilogrms. of sulphur | 12 | 5·310 | 0·462 |
| 200 kilogrms. of sulphur | | 5·745 | 0·574 |
| 300 kilogrms. of sulphur | | 5·115 | 0·426 |

are interesting chiefly from another point of view. They demonstrate that in suitable proportions sulphur can favour carbureted nutrition of plants. In suitable proportions, variable with each species (200 kilogrms. per hectare for haricots and 300 for peas) sulphur favours formation of starch and photo-synthetic action, the latter being the consequence. Messrs. Mazé and Demolon have already demonstrated that sulphur is necessary for development of chlorophyll, its absence causing chlorosis. In consequence of this action on the green pigment, decomposition of atmospheric carbonic gas is stimulated, carbon is fixed in larger quantities and reserved in form of starch. Researches on the gaseous exchanges of assimilation would probably confirm this assertion. Thus, according to these observations, in addition to the value of sulphur as an aliment in form of sulphuric acid and catalytic agent in assimilation of soil nitrogen, we may add the influence, also essential, exerted on fixation and atmospheric carbon in consequence of its action on chlorophyll. Owing to this multiple action, its employment in agriculture deserves exhaustive study.—*Comptes Rendus*, January 3, 1921.

Catalytic Hydration of Nitrites.—Nitrites, as is known, can be prepared by ctalysis of a mixture of an acid and ammoniacal gas, in contact with a dehydrating catalyser like thorine or alumina. The same reaction also occurs with ether salts in which the group CO loses its atom of oxygen which forms water with ammoniacal gas. Now we know that a catalyser will accelerate the speed of a reaction; it also accelerates the inverse reaction. One might, therefore, think that nitrites would undergo catalytic hydration in contact with thorine and alumina, and be thus transformed into acid $RCN+2H_2O=RCO_2H+NH_3$. This was demonstrated in experiments made by M. A. Mailhe.—*Industrie Chimique*, January, 1921.

Price of the Unit of Nitrogen in Chemical Manures in Spain.—The *Informacion Agricola* gives the following observation in favour of Chile nitrate. The difference in the effects of various nitrogenous fertilisers equally rich in nitrogen are not comparable considering that the nitrogen in some, like nitrates, is better utilised by plants, not undergoing any transformation before being

assimilated, nor losses in the soil through decomposition and the atmosphere, whereas in fertilisers which contain nitrogen in ammoniacal form, or other more complex forms like cyanamide, the losses are considerable, and thus with equal percentages the effects of nitrates are greater than those of other nitrogenous manures. Consequently, the prices of nitric nitrogen is always greater than ammoniacal nitrogen. Nevertheless, existing circumstances in the markets make the nitric nitrogen of nitrate of soda the cheapest in Spain. Taking the quotations in the markets of Valencia and Barcelona, for all the nitrogenous chemical manures we have nitrate of soda, 4 pesetas; granular cyanamide (only practical form of this fertiliser), 4·47 pesetas; sulphate of ammonia, 4·63 pesetas; nitrate of lime, 5·04 pesetas. To make this calculation, we took the average guaranteed percentages of all of these fertilisers, viz., 15 to 16 for nitrate of soda, 19½ to 20½ cyanamide, 20 to 21 sulphate of ammonia, and 12 to 13 nitrate of lime.—*Revista Minera*, January 8, 1921.

Vanadium in Steel.—A method for analysis of vanadium in steel, by M. E. Jaboulay is as follows. The metal being dissolved in sulphuric acid, the vanadium, and eventually chromium, are transformed into vanadic and chromic acids by potassium permanganate. Chromium, if necessary, can be titrated with ferrous sulphate and permanganate. The vanadium is estimated by adding small measured quantities of ferrous sulphate to the solution to a slight excess. When a blue colour appears, all the vanadium is in form of hypovanadic sulphate, and the solution contains a slight excess of ferrous sulphate, which must be destroyed, so as to only leave as reducing compound the hypovanadic sulphate, easily titrated with a permanganate liquor. The ferrous sulphate is destroyed by an excess of potassium bichromate. The chromic acid thus produced acts slowly on the greatly diluted hypovanadic acids, and titration can be made with permanganate before it exerts its oxidising action; however, titration should be promptly made after addition of bichromate.—*Génie Civil*, February 5, 1921.

Researches on the Action of Guanol.—Guanol is a fertiliser obtained by methodic fermentation of peat bathed with vinasse from distillation of beet molasses, under the action of micro-organisms, which produce ammonification of the nitrogenous elements (especially betain). The product is then dried; it contains 3·5 per cent nitrogen, and 7 to 8 per cent potash. Results of experiments demonstrate that (1) the effects of guanol are very slight in pots, being about equal to percentage of nitrogen in the fertiliser; (2) In the case of potatoes, in a clay soil, 6 parts guanol gave an increase of 28·7 in the crop; (3) There was no favourable effect with beet in heavy clay soil. Thus the action of guanol is not clearly specified, and new researches are necessary.—*Chimie et Industrie.*

Chemical Mechanism of the Assimilation of Carbonic Gas by Green Plants.—The existence of hydroxylamine in leaves is made certain by transformation of the ammonia into oxygenated compounds of nitrogen and *vice versâ*. These transformations comprise numerous intermediary compounds. Hydroxylamine must figure in this double series because the phenomena of oxidation and reduction realised by the living cell occur gradually, and only regard a single atom of oxygen in each stage. The experimenter, M. Mazé, has not succeeded in bringing hydroxylamine into evidence in nitrifying or denitrifying mediums. This does not mean, however, that this will not be done by aid of a suitable device. It is probable that hydroxlamine combines with the aldehydes and cetones to give oximes, and it is by virtue of this property that it acts as examination of facts shows. The existence of hydroxlamine is also shown by the constant presence of free nitrous acid and that, rather frequent, of hydrocyanic acid, two derivatives of oximes.—*Comptes Rendus*, January 17, 1921.

## New Patents.

This List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W.C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

6897—Du Pont de Namours & Co., E. I.—Cellulose ester compositions. March 2nd.
6783, 6784—Eustis, A. H.—Recovering sulphur dioxide from furnace gases, etc. March 1st.
6679—Grainger, J. E.—Apparatus for drying solid chemicals. Feb. 28th.
6686—Hansford, J. B.—Apparatus for drying sulphate of ammonia, etc. March 1st.
7045—Kelly, A.—Manufacture of borax and boric acid. March 3rd.
7830—Caspari, W. A.—Manufacture of benzene mono sulphonic acid. March 12th.
7966—Dieenthalero.—Manufacture of molybdenum metal or its alloys. March 12th.
7597—Goldschimdt, V. M.—Manufacture of magnesium chloride. March 9th.
7879—Jones, B. D.—Production of alkali pentaborates direct from boron ores. March 12th.
7569—Little Inc., D. A.—Cellulose derivative and process of preparing same. March 9th.

*Specification published this Week.*

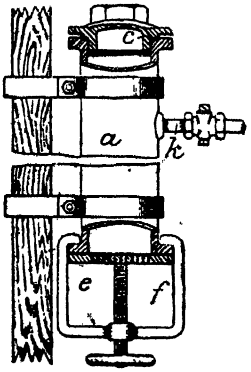
147530—New Jersey Zinc Co.—Production of metal oxides and other compounds of metals.
159337—Pascal, P.—Process and apparatus for the manufacture of liquid sulphurous acid from dilute sulphurous acid gas.
136158—General Chemical Co.—Production of oxides of nitrogen and a catalyzer therefor.
143260—Lilienfield, L.—Process of manufacture of dialkylsulphate.
159568—Ballantine, W. B.—Production of ferro-chrome alloys.
159587—Bolton, E. R. and Lush, E J.—Neutralisation of fatty acids in fats and oils.
159659—Collins, J. J.—Purifications of tin or the production of tin salts from crude tin.
139470—Kilburn, B. E. D.—Removal of iron from solutions of aluminium nitrate, sulphate or chloride.
145709—Krupp Akt. Ges. F.—Process for producing low carbon ferro-chromium.
152643—Zack, M.—Processes for separating oxygen and nitrogen and apparatus therefor.

*Abstracts Published this Week.*

*Acetic Acid.*—Mr. H. Dreyfus of Pall Mall, Westminster, has obtained a Patent No. 156916 for an improved process of obtaining acetic acid The ferric oxide employed as a catalyst in the manufacture of acetic acid by the oxidation of liquid acetaldehyde, is prepared by precipitation from a ferric salt solution, followed by heating to a temperature between 310-500° C. Its catalytic activity is stated to be enhanced thereby. Sodium acetate may be associated with a ferric oxide but only in a quantity not exceeding about double the amount of ferric oxide present

*Sulphuric Acid.*—Mr. P. Parrish and the South Metropolitan Gas Co., of Old Kent Road, have been granted a Patent No. 156328 for an

improved process and apparatus for obtaining sulphuria acid. Sulphuric dioxide is bubbled through nitrous vitriol near the surface, the depth of seal not exceeding ¼in. The apparatus shown comprises a tank *a* divided into compartments by partitions *b* supported on columns *c* and having serrated lower edges as shown in Figure. Sulphur dioxide is passed in at one end at *e*, bubbles through the liquid under the serrated edges and escapes at the other end at *f*. Stirrers may be provided below the level of the partitions.

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THE CHEMICAL NEWS.

VOL. CXXII., No. 3181.

## SRIVASTRA'S HYPOTHESIS:* A CRITICISM AND AN APPRECIATION.

By H. T. F. RHODES.

SOME difficulties of the electronic conception of the constitution of matter have been, from the beginning, evident; and it would seem that they do not tend to decrease. This does not mean of course, that the theory is untenable, but there seems to be a growing tendency to exaggerate its claims to unqualified acceptance.

At least Srivastra has shown that the electronic theory of matter is not without an alternative; and this alternative, whatever difficulties it may present, certainly breaks new ground.

It is supposed that aether is atomic and not continuous· and the difficulty, therefore, becomes an ultimate question; since it must be allowed that if this could be established, the cause of all phenomena, whether of matter or of force, must be sought in aether—the cause of causes; so that it appears that there is not one hypothesis, chemical or physical, that will remain unaffected.

In the domain of physics, this statement will more in particular apply; since without the original conception of aether—that of a continuous medium—part of the modern superstructure of physical science tumbles incontinently to the ground. It is because of this that definition must ultimately be applied in other directions that that of the structure of atoms; for, until now, matter has been matter, and aether has been aether; and the assertion that aether is matter will, without careful definition, lead to that very confusion which the new hypothesis has been designed to avoid. Further criticism is undesirable, for it is partial to criticise in general terms a theory which has a particular application, and which may, when fully developed, be found applicable to all cases that may fall within its scope.

It is supposed that "matter is aether condensed"; and that "electricity is aether in motion." This is excellent, for it maintains that matter and force, despite their common origin, differ; and a fundamental distinction is therefore recognised that it seems desirable, at present, to preserve. It cannot be denied that "the aggregate of fixed electrons" of the electronic hypothesis is unconvincing, and it introduces an element that borders upon the inconceivable.

Srivastra claims that the particles of aether in motion constitute the negative electrons, but he denies the existence of the positive electrons. Even a superficial knowledge of the electronic theory of matter suffices to make some of its difficulties manifest; but the extracts from Prof. Berthond's paper seem to make the case for the positive electron very weak indeed, since it is maintained that "an electron appears as a corpuscle of electricity, devoid of any basis of matter, in the ordinary sense of the word it is at one and the same time the elementary particle of negative electricity, and an elementary particle of matter." Some such conclusion as this is certainly inevitable, but it involves a verbal contradiction, at least; and one so preposterous as to make the statement manifestly absurd.

It has been claimed for the theory of electrons that it has but amplified Franklin's hypothesis, but it must not be forgotten that the latter preserves a more definite distinction between the two kinds of electricty; or rather there is but one "positive fluid" and the "matter". The positive together with some negative electrons have been defined as matter, and in case of hydrogen, it would seem that one positive electron constitutes the nucleus; the resulting confusion is inevitable.

Srivastra seems to agree more nearly with Franklin; but the latter's positive "fluid" has become the negative electron; a necessary inversion which agrees with the electronic hypothesis. There seems to be some verbal confusion, however, in the manner that in the first place it is said that: "Electricity is aether in motion"; and later that "Negative electricity is produced by the motion of indefinitely small aether particles." This is open to more interpretations than one; and it might be construed to mean the very opposite of that which Srivastra desires to maintain. But that aethereal particles in motion are particles of electricity, *i.e.*, negative electrons, is doubtless meant.

The assumption that the condensed nucleus, by rotation about its own axis in one direction, generates positive electricty, and that the negative particles are in motion around the nucleus, but in the opposite direction, is convincing and satisfactory.

The real difficulty of the new theory lies in the fact that it may be difficult to restrain; in fine, aether has been made an element, and therefore, will not subordinate itself to its original function; while on the other hand, since its atomic weight is supposed to be zero, it will not subordinate itself to the laws of the other elements; and for such an element as this, insubordinate seems scarcely too strong a term. These difficulties are not necessarily insurmountable, but a more extensive survey is required; and it is hoped that before long, this matter will be again before us, for the question is interesting, and deserves, therefore, a detailed discussion.

* CHEMICAL NEWS, cxxii., No. 3172.

## NOTES ON THE ELECTROLYTIC REDUCTION OF GLUCOSE.*

By ALEXANDER FINDLAY and VERNON HARCOURT WILLIAMS.

THE possibility of reducing glucose electrolytically has attracted some attention in recent years but the results obtained are somewhat conflicting. Thus O'Brien Gunn [D.R.P. 140318 (1900)] states that glucose dissolved in sulphuric acid of 1-3 per cent concentration, can be reduced electrolytically using graphite electrodes and a cell with a diaphragm, the current density at the cathode being 0·15 amp. per square decimetre. A yield of manitol (?) amounting to 98 per cent of the theoretical is claimed to have been obtained.

* A Paper read before The Faraday Society, Tuesday, March 22, 1921.

W. Löb (*Biochem. Zeitschr.*, 1909, xvii., 132; xxi., 102; *Zeitschr. Elektrochem.*, 1910, xvi., 1) on the other hand, failed to obtain this satisfactory result, and was led to conclude that both the anodic and cathodic electrolysis of glucose leads to an equilibrium between glucose, a pentose, formaldehyde, and lower carbohydrates, the cathodic reduction causing the equilibrium to shift in favour of the production of the lower compounds.

As the reduction of glucose to the corresponding hexahydric alcohol is in itself a process of importance, it seemed worth while to investigate the electrolytic process more fully, and, more especially, to study the effect on the reduction of variation of the temperature, current density, and current concentration. Although, as the result of our investigation, negative results, as regards the production of hexahydric alcohol, have been obtained, we desire to communicate some notes on our work which may prove of value in connection with this problem.

The method and apparatus employed were essentially those used by Tafel (*Zeitschr. Physikal. Chem.*, 1900, xxxiv., 187), in his studies on electrolytic reduction. A closed cell was employed as cathode chamber, and the volume of hydrogen evolved during electrolysis was compared with that evolved from a hydrogen voltameter placed in series with the electrolytic cell. The difference in the volume of hydrogen evolved in the two cells represents the amount of hydrogen used up in the reduction.

The glucose used was "extra pure" glucose supplied by British Drug Houses, Ltd. Examined polarimetrically it gave a rotation corresponding with a purity of 99·87 per cent.

In most of the experiments lead electrodes were employed, and as Tafel has shown that the presence of metal impurities has a very unfavourable influence on the cathodic reduction, care was taken to ensure the purity of the lead electrodes employed. The purity of the lead was tested by analysis of the surface layers and the results of analysis were also confirmed by a repetition of Tafel's experiments on the reduction of caffein. This control served also to show that our method of working was satisfactory.

In the first series of experiments, carried out at the ordinary temperature, 14° to 17°, the current density employed was 0·16 amp. per 100 square cm., and the solution contained 1, 3, and 10 per cent. of glucose in 3 per cent. sulphuric acid. In all cases the rate of absorption of hydrogen fell off rapidly, practically to zero, and the total amount absorbed corresponded with no more than about a 2 per cent. reduction of glucose (see Table I.). In the following table, *t* is the total time in minutes from the commencement of the experiment; T, the time in minutes from the commencement of the experiment to the middle of each period during which successive readings of the burette were made; *e*, the volume in cc. of gas evolved in the electrolytic cell; *v*, the volume in cc. of gas evolved in the voltameter; E, the rate of evolution of gas in the electrolytic cell in cc. per minute; V, the rate of evolution of gas in the voltameter; R, the rate of absorption of gas in cc. per minute.

TABLE I.

Cathode liquid: 1 per cent, solution of glucose in 3 per cent sulphuric acid. Current density: 0·16 amperes per 100 square cm.

| *t*. | T. | *e*. | *v*. | E. | V. | R. |
|---|---|---|---|---|---|---|
| 0 | 2 | 0 | 0 | 0·125 | 0·300 | 0·175 |
| 4 | 6 | 0·5 | 1·2 | 0·187 | 0·262 | 0·075 |
| 8 | 10 | 1·25 | 2·25 | 0·212 | 0·312 | 0·100 |
| 12 | 14 | 2·1 | 3·5 | 0·250 | 0·300 | 0·50 |
| 16 | 18 | 3·1 | 4·7 | 0·262 | 0·287 | 0·025 |
| 20 | 22 | 4·15 | 5·85 | 0·250 | 0·287 | 0·037 |
| 24 | 26 | 5·15 | 7·0 | 0·262 | 0·300 | 0·038 |
| 28 | 33 | 6·2 | 8·2 | 0·270 | 0·285 | 0·015 |
| 38 | 45 | 8·9 | 11·05 | 0·271 | 0·285 | 0·014 |
| 52 | 57 | 12·7 | 15·05 | 0·280 | 0·285 | 0·005 |
| 62 | 67 | 15·5 | 17·9 | 0·275 | 0·290 | 0·015 |
| 72 | | 18·25 | 20·8 | | | |

The total volume of hydrogen absorbed in the above experiment over the period of 72 minutes was only 1·42 cc. at N.T.P.

Similar results were obtained on commencing the electrolysis with a peroxidised lead cathode, and also when the sulphuric acid was replaced by sodium bisulphate as electrolyte.

*Influence of Temperature.*—On carrying out the electrolysis at a temperature of about 44°, no better results were obtained. The influence of temperature was found to be practically inappreciable; if anything, the hydrogen absorption was diminished.

*Graphite Electrodes.*—On using electrodes of gas carbon or of Acheson graphite the results were similar to those obtained with a lead electrode.

*Current Density and Current Concentration.*—In general, reduction of the cathode current density is accompanied by a slight increase in the efficiency of electrolytic reduction, but although we carried out an experiment with a current density somewhat lower than that previously employed (0·102 instead of 0·16 amp./sq. dcm.), no appreciable improvement was observed. It has, however, been shown by Tafel (*loc. cit.*), that current concentration (current per unit volume of solution), has a greater influence than current density. Experiments were therefore carried out in which the current concentration was varied between the limits of 0·04 and 0·444 amps per 100 cc. The results obtained showed that with increase of current concentration, the absorption of hydrogen also increases but, as in previous experiments, falls off rapidly with time.

During the progress of these experiments it was observed that the cathode solution, after electrolysis, possessed a sharp aldehydic odour, and the cathode was found to be coated with a film of slimy appearance. This film was soluble in alcohol. As it was thought that the production of this film might be the cause of the rapid falling off of the volume of hydrogen absorbed by the depolariser, experiments were carried out in which the same solution was subjected to repeated electrolysis, the cathode, after each run, being treated with boiling alcohol to remove the film produced. After each treatment of the cathode it was found that a further absorption of hydrogen took place,

but that this absorption again rapidly fell off to zero. Using a current concentration of 0·444 amps. per 100 cc., and a cathode solution of 20 per cent glucose in 5 per cent sulphuric acid, the following successive absorptions of hydrogen were realised: 28·5, 8·1, 32·2, 52·8, 30·2, 24·1, and 23·5 cc. The total absorption amounted therefore to 199·4 cc., or 40·1 per cent of the theoretical amount. During these experiments, which extended over several hours, a considerable loss of glucose took place by diffusion from the cathode cell. In the most favourable case, where the highest current was employed, the loss amounted to nearly 30 per cent; where lower currents were employed and the duration of the electrolysis was therefore greater, the loss by diffusion was of course also greater. Attempts to diminish diffusion by use of a membrane of copper ferrocyanide deposited in the wall of the porous cathode cell, were not successful.

Since the foregoing experiments seemed to indicate that a considerable proportion of the glucose had been reduced, an attempt was made to isolate the supposed product of reduction, the hexahydrate alcohol. The solution was neutralised with chalk to remove sulphuric acid, and was then evaporated on the water bath. The syrupy liquid was dissolved in concentrated hydrochloric acid, and the acid solution shaken with benzaldehyde and allowed to stand for several days. By this means, mannitol or sorbitol, if present, can be precipitated as a condensation product with benzaldehyde (Meunier, *Compt. Rend.*, 1888, cvii., 910). No such compound, however, was obtained, and we are therefore driven to conclude that no appreciable amount of hexahydric alcohol was produced in our electrolytic experiments.

On examining the alcoholic washings from the cathode, a lead salt was isolated which, on analysis, was found to be lead formate. Formic acid was also found in the cathode solution after electrolysis. The production of this acid in the electrolytic reduction of glucose is mentioned by Löb (*Zeitschr. Elektrochem.*, 1910, xvi., 1), who states that glucose decomposes into formic acid and a pentose. The presence of pentose in the solution we detected by the furfuraldehyde test.

Further evidence of the production of formic acid was obtained from an analysis of the gas evolved at the cathode during electrolysis. This gas was found to be not pure hydrogen but to contain about 4 per cent of carbon monoxide, produced, presumably, by a decomposition of formic acid. The percentage of carbon monoxide varied somewhat during electrolysis, being greater during the earlier than during the later stages of the electrolysis. Although the destructive reduction of glucose with production of formic acid and a pentose does not appear to take place to a very large extent, the formation of these compounds may play an important part in the process of electrolytic reduction if, as seems probable, it is the formic acid which leads to the formation of the film on the cathode with consequent diminution or prevention of further reduction.

As a result of our experiments, which are in harmony with the results obtained by Löb, we are forced to conclude that, contrary to the claims of O'Brien Gunn, no hexahydric alcohol is produced in the electrolytic reduction of glucose.

# OVERGROWTHS ON DIAMOND.*

By J. R. SUTTON.

## *The Affinity between Diamond and Carbonate of Lime.*

"FORMERLY the diamonds were picked out from the concentrates by means of the keen eyes of skilled natives, but the process has been vastly simplified . . . by the remarkable discovery made in 1897 by F. Kirsten of the De Beers Company, that of all the heavy constituents of the blue ground, diamond alone, with the exception of an occasional corundum and zircon, which are easily sorted out afterwards, adheres to grease more readily than to water. In this ingenious machine . . . the concentrates are washed over a series of galvanised-iron trays, which are covered with a thick coat of grease. The trays are slightly inclined downwards, and are kept by machinery in constant sideways motion backwards and forwards. So accurate is the working of this device that few diamonds succeed in getting beyond the first tray, and none progress as far as the third."

This account, which contains nearly all that is necessary by way of preface, is extracted from G. Herbert Smith's charming "Gem Stones," 1912, p. 148. Evidently the secret of the process, as Lawn has said, is surface tension Common minerals can easily be wetted, whereas diamond cannot be; and because of the wetting the grease cannot touch the mineral surface, whereas it can touch the dry diamond.

According to G. F. Williams "only about one-third of 1 per cent of diamonds is lost by the first table, and these are recovered almost to a stone when the concentrates are passed over the second table" ("The Diamond Mines of South Africa," 1902, p. 380).

J. Stewart reports further that for the six months July to December, 1909, out of 1,211,552 carats of diamonds recovered at the De Beers Company's pulsator, all but 1,249 carats were caught on the first tables—an efficiency of 99·9 per cent.

But it is a curious fact that while diamonds of all kinds, including bort, from the blue ground adhere readily to the grease tables, those from the surface yellow ground are much less easily caught. Some years ago a parcel of diamonds from the Wesselton Mine yellow ground was handed to me for examination. Some concentrates from the yellow ground had been passed over the grease tables with the following result:—

| | Carats caught. | Per cent. |
|---|---|---|
| First table ... ... ... ... ... ... | 241 | 50·52 |
| Second table ... ... ... ... ... ... | 90 | 18·87 |
| Third table, and final dry sorting of rejected concentrates ... ... ... | 146 | 30·61 |
| | 477 | 100·00 |

That is to say, instead of a loss of between one-tenth and one-third per cent (the values quoted above), only about half of the diamonds were caught on the first table—a result scarcely better than an electrostatic separator would give. Clearly it was lucky that the grease tables were

* From the Transactions of the Royal Society of South Africa.

not thought of in the early days of Kimberley, when nothing but yelow ground was being worked for, had they been tried then, that excellent invention would probably have passed stillborn into oblivion.

In the matter of the anomalous behaviour of the yellow-ground diamonds the problem to be solved was unique, inasmuch as there was no outside analogy for a guide. To begin with, there was nothing to show whether the surface of yellow-ground diamond was essentially different from that of blue-ground diamond, or whether the anomaly arose from some disturbing factor in the matrix. As to the former alternative, there was a prevalent belief that the surfaces of diamonds found in the early days of Kimberley were on the whole more brilliant than those obtained later, in the deep workings. As to the latter alternative, it appears that the soapy-feeling substance lining the blue-ground matrix of diamond has not quite the same constitution as adjacent blue-ground has. This point will be referred to again.

The first step in the attempt to solve the problem was made by screening the diamonds caught on the three different tables into series of sizes. From the results it was ascertained that, generally speaking, the larger diamonds tended to adhere to the grease on the first table better than the smaller ones did, those caught on the third table not often exceeding a quarter of a carat each. There was, moreover, a marked difference in the behaviour of the smaller diamonds with respect to the tables, for while those caught on the third table, or dry sorted afterwards, were largely of good shape with no specially great proportion of cleavages and splinters, those caught on the first table were mostly irregular or broken pieces. Hence it seems that a still larger quantity would have been lost by the first table if the normally great percentage of Wesselton cleavage were less. Two possibilities were thus suggested :—

(1) The larger diamonds stick better than the smaller ones do because their weights being great relatively to their surfaces they travel more slowly in a given current of water, and so can sink mechanically more heavily into the grease. Here it may be noted that pieces of iron and heavy minerals sink into the grease not because of any attribute of surface tension, but because the current of water flowing over the tables is insufficient to overcome gravitation.

(2) Apart from that, some peculiarity of surface seemed involved whereby fractured faces were more adhesive than natural faces. On the other hand the sharp edges of the fractured faces can plunge mechanically into the grease with more facility than natural edges can.

Under magnification, however, no characteristic difference could be detected either between the surfaces of the diamonds taken from the different tables, or between the surfaces of the non-adhesive yellow-ground diamonds and the surfaces of ordinary adhesive blue-ground diamonds. Some specific gravity tests, also, reveal no differences worth mention.

Since only a few diamonds from the blue ground are normally lost by the first grease tables, it remained to examine typical specimens of blue and of yellow ground, in order to determine whether any accountable peculiarities exist in the respective matrices which might be communicated to a diamond surface. Competent geologists are pretty unanimous that the yellow ground, which may go down even to 70ft., is simply blue ground in a weathered condition, and contains the same minerals in due proportion" (W. H. Penning, "Gold and Diamonds," 1901, p. 4). But unanimity in the case of the diamond is never evidence, and, for the most part, judging by the strong family likeness of the various accounts, each high expert quotes without question from some higher expert. At any rate, some samples of blue ground, yellow ground, and so-called "limestone" from the original overburden, were obtained for testing purposes from the Wesselton mining area. So far as could be seen the samples of yellow ground were typical and clean. The blue ground had other matter mixed up with it, which had probably been scraped up from the depositing floors by the shovel. It could only be guessed whether the "limestone" was an average sample of its kind. It was a spongy-looking stuff of rather low specific gravity (?altered blue ground, or dolomitic), and to casual inspection carried particles of yellow ground. Portions of each of the three kinds of ground were crushed, gently dried, weighed, treated with dilute acid, evaporated to dryness, and again weighed, with the following result :—

| | Weight before treatment. | Weight after treatment. | Loss Per cent. |
|---|---|---|---|
| Blue ... ... ... | 10·000 | 9·225 | 7·75 |
| Yellow ... ... | 10·000 | 8·650 | 13·50 |
| "Limestone" ... | 10·000 | 9·975 | 0·25 |

In the acid the blue ground effervesced strongly, the yellow ground violently, the limestone scarcely at all. A sample of hard blue from De Beers Mine, tested at the same time, gave scarcely any effervescence, while some lumps of hard and soft limestone from Kenilworth effervesced violently, leaving no great proportion of insoluble residue, so that the effervescence of the blue ground may have arisen, at any rate in part, from an admixture of a foreign carbonate. Moreover, the substance (alluded to above) lining the matrices of sundry blue-ground diamonds effervesced very little.

These rough tests seemed to supply a clue worth following towards a solution of the problem. There is more carbonate of lime in yellow ground than there is in blue ground, and the question is: Will it, when it is plentiful enough, spread itself on a diamond surface in a crust capable of being wetted? Numerous experiments were accordingly made in the hope that premised feasible natural processes might to some extent be imitated in forming such a crust. Pastes were made of the blue ground, the yellow ground and the limestone, with hot and with cold water, in which small diamonds that had adhered normally to the first grease table were enclosed for some days. Sometimes these pastes were kept wet throughout, sometimes they were dried in gentle heat, and sometimes left to dry of themselves. Finally the enclosed diamonds were taken out and run over the grease tables at the pulsator. The results were only so far encouraging that neither the diamonds from the yellow paste nor those from the limestone paste showed any particularly marked inclination to stick to the grease. But on the other hand, curiously enough, neither did the diamonds from the blue paste. Thus although all

were originally normal first table captures, the act of putting them into the different pastes had for the most part destroyed their adhesive property

Of course, only a soft and easily removable crust, at the best, can be deposited on diamonds by enclosing them for short periods in pastes of this kind. One effort was made to deposit a harder crust on four first table diamonds of about six carats each by placing them in four separate vessels with some blue, yellow, and lime ground respectively, well stirred with plenty of water, and leaving the water to evaporate slowly. This is a lengthy process, and was only partially successful. Scarcely any blue ground appeared to have attached itself to the diamond surface, though the lime and yellow were deposited in patches with some freedom. Upon roughly testing these diamonds for surface tension in water, it was found that those from the lime and yellow grounds gave much higher values per unit area of surface than those from the blue ground did, albeit a single test of this kind cannot be regarded as of much consequence. These same diamonds were afterwards passed over the grease tables: three adhered, and one, which had a fair coating of lime, rolled away.

The experiments were repeated with three good samples of virgin blue, yellow, and real limestone crust, obtained from the Kamfersdam Mine. In acid the blue gave no effervescence to speak of, while the yellow effervesced strongly, losing 20 per cent of its weight, and the lime crust violently, losing fully 60 per cent. Pastes were now made as before of the virgin blue and of the lime crust in equal quantities, and ten first table diamonds, weighing on an average about a carat a-piece, were placed in each paste. The two lots of diamonds were chosen so as to be nearly alike as possible. After the pastes had become quite dry they were broken, the diamonds were carefully extracted, soaked in water, and passed over the grease tables. Every diamond from the limestone paste rolled off as fast as the water could carry it; whereas nearly all the diamonds from the blue were caught.

Lastly, some third table and dry sorted diamonds, *i e.*, diamonds which originally were not easily caught, or even not caught at all, by the grease, adhered quite well after having been cleaned in acid.

(To be continued.)

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

*March* 10, 1921.

Prof. C. S. Sherrington, President, in the Chair.

The following papers were read :—

"*Electro-crystalline Properties as conditioned by Atomic Lattices.*" By Sir Joseph Larmor, F.R.S.

The view, confirmed on grounds of ultra-optical analysis by Bragg, that the crystal lattice is usually composed of atoms, not concentrated into chemical molecules, is considered in relation to their ionic charges. Compensating surface charges on certain types of faces of a crystal are required; and inference is drawn with regard to the texture of crystal faces. The alternative view that a bipolar molecule is the crystal-unit would seem to encounter difficulties also as regards pyro-electric effects. Dielectric excitation can be represented as *relative* displacement of the positive and negative component lattices, under the influence of an electric field. If the compound lattice has spiral features, so that the relative shifts of its various components with positive and negative charges are of screw type, chiral optical quality will be involved; a coarse numerical estimate indicates that in quartz and active liquids the twisting relative displacement of the ionic configurations is comparable in amount with their relative elongation, as would be natural in the spiral lattice. The chiral quality may reside wholly in the crystalline structure, disappearing on fusion or solution; or else the process of dielectric displacements of the positive and negative groups of ions in the crystal-unit may be also itself chiral. In either case induced static polarity could not be chiral as regards waves so long as those of light; but this process of screw displacement is operative kinetically in the optical rotation, by involving a magnetic moment of changing ionic twist induced by the alternating electric field of the radiation. The octo-polar pyroelectric quality in the faces of crystals of cubic type, explored originally by Haüy, need not now have to be referred to strains arising from irregular cooling, but a face containing both types of ions equally should now acquire no true pyro-electric charge. Double refraction induced by strain must be ascribed to bending of ionic lattice structures, as molecules could hardly bend, or in glass to fragments of such structure.

"*A Generalisation of Weyl's Theory of the Electro-Magnetic and Gravitational Fields.*" By Prof. A. S. Eddington, F.R.S.

From the notion of "parallel displacement" used by Weyl in his theory, it is shown that a tensor $*B^{\rho}_{\mu\nu\sigma}$ exists giving a measure of the world-structure at each point. The contracted tensor $*G_{\mu\nu}$, formed by setting $\rho=\sigma$, breaks up into two parts, (1) a symmetrical part which is the gravitational potential $g_{\mu\nu}$ of Einstein's theory, and (2) an antisymmetrical part $F_{\mu\nu}$ (proved to be the curl of a vector) which is identified with the electro-magnetic force. The theory explains how, notwithstanding the non-integrability of length in Weyl's geometry, there is, nevetheless, a natural gauge; and Einstein's *interval* is an absolute invariant independent of gauge, and directly comparable with other intervals at a distance, as he assumed it to be. The law of gravitation for empty space in the form finally adopted by Einstein, viz., $G_{\mu\nu}=\lambda g_{\mu\tau}$, follows at once on this theory. All the other recognised field-laws are found by identifying the physical measures with geometrical tensors which satisfy these laws identically. None of these impose any constraint on the possible varieties of world-structure; and there is no reason to introduce a physical principle of stationary action, at least so long as we do not deal with problems of electron structure. Explicit expressions for $*B^{\rho}_{\mu\nu\sigma}$ and $*G_{\mu\nu}$ are found in

terms of Einstein's gravitational tensors and a tensor $K_{\mu\nu,\sigma}$ which represents electric and electronic forces. Weyl's theory corresponds to the particular case when $K_{\mu\nu,\sigma}$ is of the form $g_{\mu\nu}\phi_{\sigma}$.

"*Spectrophotometry in the Visible and Ultra-violet Spectrum.*" By PROF. T. R. MERTON, F.R.S.

The application of the neutral wedge to spectrophotometric measurements is at present limited to the visible spectrum and the less refrangible parts of the ultra-violet spectrum. A description is given of a method by which this limitation is removed. The method involves the "crossing" of the prismatic spectrum with a diffraction spectrum, the relative intensities of the different orders in the diffraction spectrum having been experimentally determined. The method of preparing and calibrating gratings for this purpose is described. The method is applicable to the determination of the relative intensities of lines in discontinuous spectra, but is specially adapted to the study of continuous spectra, absorption spectra, and the study of broadened lines. It is suggested that the method may have a special application in celestial spectroscopy.

"*Researches upon Brown Coals and Lignites. Part I.—Heat Treatment at Temperatures below 400° C. as a Possible Method for Enhancing their Fuel Values.*" By PROF. W. A. BONE, F.R.S.

A classification of lignites is made according to their external appearance:—

(a) Woody or fibrous brown coals.
(b) Amorphous or earthy brown coals.
(c) Common or brown lignites.
(d) Black lignites.

Lignites have a moisture content varying between 10 and 50 per cent; on air-drying they usually disintegrate or crumble to powder. They are devoid of any cooking properties, and in the "dry ashless" state usually contain less than 70 per cent. of carbon and more than 20 per cent of oxygen.

Experiments were conducted on the various types of lignites — from Australia (Victoria), Burma, Canada (Saskatchewan), and Italy (Tuscany and Umbria). The method was to heat in a special form of apparatus that allowed accurate measurement of temperature and amounts of liquid and gaseous products.

On heating the lignite chemical change takes place, beginning at a low temperature of about 130° C., and progressing to a temperature at which no condensable hydrocarbons were eliminated from the fuel, termed the "practicable upgrading limit." During this period of heating, steam and carbon dioxide, with a small amount of carbonic oxide and a negligible amount of hydrocarbons, were eliminated. The gaseous products after condensation of the steam usually consisted of about 95 per cent of the two oxides of carbon.

This treatment showed a loss of between 8 and 15 per cent of its original weight at the expense of the oxygen content, which was diminished by between one-quarter and one-third of its original value. Practically the whole of the potential energy of the lignite is concentrated in the residue obtained by this "up-grading" treatment; hence it has greater calorific intensity than the original.

"*A Superior Limit to the Age of the Earth's Crust.*" By PROF. H. N. RUSSELL.

The method of determining the age of a mineral from the ratio of lead to uranium in its composition may be extended to the earth's crust as a whole. On the usual assumption, and accepting a radium content of $2{\cdot}5\times10^{-12}$ (Joly), corresponding to a uranium content of $7\times10^{-6}$, and a content of lead of $22\times10^{-6}$ (F. W. Clarke), it follows that the age of the crust does not exceed $11\times10^{9}$ years, which is reduced to $8\times10^{9}$ years, if allowance is made for thorium.

The effects of uncertainty in the assumptions are considered, and it is concluded that the earth's crust has probably existed as such for between two and eight thousand millions of years.

"*Reversal of Asymmetry in the Plutei of Echinus miliaris.*" By H. OHSHIMA.

In the normal Echinoderm larva the hydrocœle and its associated structures, which together give rise to the water-vascular system, develop on the left side of the larval body. Rarely the reversal of this asymmetry occurs, and of this a very few instances have hitherto been recorded.

This abnormality was found in more than 10 per cent of the artificially-reared larvæ of *Echinus miliaris*. It may be a result of (1) change of polarity in the egg, or (2) twin-formation, or, most probably, (3) "compensatory hypertypy," owing to the arrest in development and subsequent atrophy of the normal left hydrocœle. The right anterior cœlom is known to have the latent potentialities of producing a hydrocœle. The potentialities can probably be activated by the stimulus, due to the arrest in development of the left hydrocœle. The arrest is probably associated with the obliteration of the pore-canal, through which the hydrocœle has been communicating with the exterior.

The occurrence in much lower percentage of the double-hydrocœle larvæ and those devoid of the hydrocœle within the same culture jars can also be explained in connection with the above-mentioned third possibility. If the left hydrocœle regains its communication with the exterior, either by the reappearance of the pore-canal or by the fusion of the right and left anterior cœloms, it will continue to develop further hand in hand with the abnormally appeared right hydrocœle, so as to give rise to the double-hydrocœle larva. If the right hydrocœle fails to appear while the left hydrocœle is still deprived of its communication with the exterior, and thereby ultimately atrophies, a larva devoid of hydrocœle will result.

## THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

*February* 2, 1921.

ANNUAL ADDRESS OF THE PRESIDENT, MR. ALFRED SMETHAM.

IT has been customary in the past for the President of the Society at the Annual General Meeting to bring under survey the activities of the members

and the work and progress of the Society in the official year that sees its close at the Annual Meeting; and it thus falls to my lot to-day to review the proceedings of the past year. Following as I do in the footsteps of a long array of brilliant chemists and able administrators, I feel that the task of doing adequate justice to the subject is no light one, and I would that I could relegate the duty now imposed upon me to someone better fitted for the post; but since the address must in the main be a *résumé* of the work of others rather than an exposition of one's own views, I have greater confidence than I should otherwise feel in imposing my remarks upon you.

During the year ending December 31, 1920, the total number of members, including 11 honorary members, has increased from 448 to 454. New members elected number 26, while we have lost 8 members by death, 8 members have resigned for various reasons, while three members have been removed for non-payment of their subscriptions.

The names of the deceased members whom we mourn are: William Beaverly Cowie, Walter William Fisher, James Wright Gatehouse, Alfred Howard, John Ruffle, Robert Tervet, Elwyn Waller (of New Jersey, U.S.A.), and Samuel Archibald Vasey.

Obituary notices have appeared in the pages of the *Analyst* of Walter William Fisher and James Wright Gatehouse.

Walter William Fisher was one of the oldest members of the Society of Public Analysts, and acted as its President in 1889 and 1890. He was Public Analyst for the counties of Oxford, Berks, and Bucks, as well as for the City of Oxford, which posts he held for nearly 40 years, and to within a week of his death carried out actively the duties appertaining to the posts. We deplore his death, and the many members of the Society who knew him have to lament the loss of a staunch friend.

James Wright Gatehouse died on October 16, 1920, at Bath, at the age of 79. In 1877 he was appointed Public Analyst for the City of Bath, and, eleven years later, Public Analyst for Wiltshire. In addition to his duties as Public Analyst, he carried on a private practice, and did much good work in various investigations.

By the death of John Ruffle I have lost a friend of over 40 years' standing. Although of a gentle and retiring nature, he was a man of many parts, and did much useful work. He will be best remembered, perhaps, as the originator of the Ruffle method for the estimation of nitrates by the combustion process.

During the session 23 papers were read, while 32 papers and 8 "notes" were published in the *Analyst.*

During the year 1920, the following papers appeared in the pages of the *Analyst*:—

"A New Method for Detecting Adulteration in Butter and for Estimating Fats of the Coconut Group." By George Van B. Gilmour

"A New Process for the Estimation of Arsenic, with Notes on the Chemistry of the Marsh-Berzelius Process." By B. S. Evans.

"The Estimation of Mercury." By H. B. Gordon.

"An Investigation into the Composition of the Unsaturated Hydrocarbons present in Coal Gas." By F. S. Sinnatt and L. Slater.

"The Estimation of the Available Oxygen in Sodium Perborate and in Perborate Soap Powders." By H. Trickett.

"The Differentiation between Poor and Adulterated Milk." By T. R. Hodgson.

"Machine for Washing Precipitates." By Eric Sinkinson.

"The Detection of Finger-Prints on Documents." By C. Ainsworth Mitchell.

"Photomicrography with Simple Apparatus." By Thomas J. Ward.

"Note on the Solubilities of Theobromine." By Raymond V. Wadsworth.

"A New Method for the Estimation of Methyl Alcohol." By S. B. Schryver and Cyril Christian Wood.

"Note on Opium Poisoning." By E. H. Hankin and D. Chatterji.

"An Examination of Certain Milk Records." By G. W. Monier Williams.

"An Improved Slide Rule for Dairy Calculations." By H. Droop Richmond.

"The Examination of Chinese Crude Camphor." By E. R. Dovey.

"Estimation of the Age of Ink in Writing." By C. Ainsworth Mitchell.

"A Rapid Volumetric Method for the Estimation of Iron, Applicable in the Presence of Hydrochloric Acid, Phosphorus, Oxy-acids, and Organic Matter." By H. Droop Richmond and Edith M. Ison.

"The Estimation of Nitroglycerin." By H. Droop Richmond.

"The Effect of Pressure upon the Polenske and Reichert-Meissl Values." By Vincent H. Kirkham.

"The Composition of Milk in British East Africa." By Vincent H. Kirkham and A. C. Barnes.

"Note on the Refractive Indices of Mixtures of Isopropyl Alcohol and Acetone." By Dorothy Muriel Palmer.

"The Estimation of Codeine." By H. E. Annett and Haridas Sen.

"The Influence of the Free Fatty-Acid Content in the Valuation of Chinese Wood Oil by the Browne Polymerisation Test." By Philip E. Jameson.

"Apparatus for Evolution Methods of Analysis." By E. R. Dovey.

"An Improved Form of U-Tube." By E. R. Dovey.

"A Study of the Determination of Potassium as the Perchlorate, and the Separation from Sodium, etc." By R. Leitch Morris.

"Notes on Rubber Analysis." By A. R. Pearson.

"An Improvement in the Haldane General Air Analysis Apparatus." By Robert C. Frederick.

"The Gravimetric Estimation of Bismuth as Phosphate and its Application in Ore Analysis." By W. R. Schoeller and E. F. Waterhouse.

"The Position of Analytical Chemistry in France." By L. Cofman.

Statutory Standard for Ghee." By T. K. Ghose

In addition to the papers published, the "Notes" on analytical methods and other matters have proved exceedingly interesting and useful, and I welcome this comparatively new departure as a distinct boon to analysts generally.

During the year thirty-two books have been reviewed in the pages of the *Analyst*. In my opinion these Reviews have been wholly admirable. They have been fearlessly and faithfully done by experts in the subjects reviewed whose judgment is reliable. They have brought to my notice some books of sterling value, and in other cases have saved my pockets from being depleted of cash and my bookshelves from being overloaded with trash.

Before leaving the subject of the publications in the *Analyst*, I cannot refrain from mentioning the loss which the Society has sustained by the resignation of Mr. Julian L. Baker as Editor of the *Analyst* to assume the Editorship of the *Journal of the Institute of Brewing*. Mr. Baker has been Editor of the *Analyst* for 13 years, during the whole of which time the Journal has been admirably conducted, and each succeeding year, thanks to his assiduous attention and genius, has seen, I think it will be generally admitted, an improvement on the previous ones. Bowing to the inevitable, we very reluctantly relinquish him, knowing that what is our loss is his and others' gain.

Fortunately, we have been able to secure in Mr. Baker's stead a new Editor, Mr. C. A. Mitchell, who is well-known to us by his scientific abilities, his literary merits, and his devotion to the Society and its publication. Mr. Mitchell as an author has a high reputation, and he has been an Abstractor for the *Analyst* for a long time. To him we may look with confidence to maintain the high standard and traditions of our Journal.

It was with much satisfaction that we welcomed back our Hon. Treasurer, Mr. E. Hinks, who has returned safe and sound to resume his duties. At the same time I ought to voice the thanks of the Society to Mr. E. W. Voelcker as Acting Treasurer during Mr. Hinks' absence.

Before leaving this part of my subject, I should like to take this opportunity of congratulating one of our past Presidents (Mr. A. Chaston Chapman) on his election as a Fellow of the Royal Society.

We have to regret the prospective loss, by absence abroad—we hope for a comparatively short period only—of our old and faithful friend, Otto Hehner. Mr. Hehner is too well known to all of us to render it necessary for me to recall to your minds all the posts he has held and all the work he has done to further the interests of the Society and to advance the cause of analytical chemistry.

Of the many questions which have come before your Council for consideration, one has been a motion to ascertain whether the present somewhat cumbrous title could not be modified in such a way as to include all the present members, while at the same time the prestige of nearly 50 years' strenuous work and endeavour under the old title could be preserved. Legal advice has been taken, and I understand that there is no legal difficulty in altering the name of the Society, and at the same time of preserving the privileges which we at present enjoy. It is not an easy matter to select a title which will be at once descriptive, inclusive, and euphonic; but there should be no insuperable difficulty in finding a solution.

The original title of the Society of Public Analysts has become so widely known and respected that in many ways it seems a pity to hide its identity under a new title; but as the term public analyst is limited by Act of Parliament to those analysts appointed under the Food and Drugs Act—and cannot, therefore, be appropriated by practising analysts generally—there seems no alternative but to change the name or continue as at present. Doubtless some happy solution of the problem will be evolved, but of the suggestions hitherto made none seem quite to meet my æsthetic taste. There is a crispness about our original title which seems to arrest the attention at once.

The fact that the proportion of analysts other than public analysts has been steadily increasing renders the alteration in the title, if it is to be descriptive of the objects of the Society, the more necessary, and as the number of public analysts is practically stationary, while the analysts engaged in general practice and in connection with trade and manufactures are steadily increasing, and, with returning trade and prosperity, are bound to increase rapidly, it seems to me that if the alteration in title is necessary or desirable, the present is an opportune time to make it

I have said that the proportion of analysts other than public analysts is in the future likely to increase at a rapid rate, and I am basing the statement on a careful observation of commercial and manufacturing conditions for a period of over 40 years. When I went into practice my work consisted for the most part of analyses to assist in the control of manufacturing processes, or to help purchasers to make a selection of produce sold practically on a flat rate; and very few of the analyses were sent under contracts, the price to be decided by the contents of the valuable constituent or constituents, as the case might be.

As the years went on and rule of thumb in manufactures was replaced by more scientific control, purchasers insisted on safeguards, especially when buying forward, and by gradual evolution in nearly every branch of industry. Safeguards in contracts are inserted, and in many instances these safeguards take the form of restrictions based upon analytical control.

Concurrently with the altered conditions in manufacturing methods, and the greater demand for more definite specifications with regard to quality, especially when the goods in question have been bought to arrive, the demand has arisen for increasing the safeguards against any inferiority in the produce which may be tendered in fulfilment of a contract. This desire on the part of the more progressive merchants and manufacturers has brought into existence a considerable number of combinations of diverse interests, who, forming themselves into associations representing their respective trades or businesses, have generally controlled the transactions, especially in the case of our overseas trade. Each year sees the framing of innumerable new contract forms, and the modification of old ones, and with the increase in the stringency of the demands on the part of buyers there has been necessarily an increase in the volumes of work falling to the lot of analysts in general. And if I read the signs of the time aright it seems to me that the tide having begun to flow in this direction it will continue to do so until a high-water mark has been reached and practically the whole of our commerce brought

under scientific control. The employment of men of exceptional talent by companies and associations for the pursuit of pure research, in contradistinction to the control of manufacturing processes or business transactions, is evidence sufficient to indicate that our leaders of commerce and industry are rapidly realising, thanks partly to work done by chemists and other scientists during the war, that research work is not only a necessary adjunct to a successful business enterprise, but it is at the same time a highly profitable investment.

And I am glad to see this tendency on the part of leading business men to call to their assistance the best brains of our profession, because it must inevitably have a leavening effect on the general mass of business men who, in the past, have regarded chemists, not as a necessary controlling influence in the factory or in business, but as an unavoidable adjunct to the business side of their concerns.

The admirable work done during the war by so many members of our profession, both at home and abroad, and the important part played by the investigations and work of our chemists in finally winning the war, has brought home to the nation at large the immense importance and possibilities of chemistry, not only in fostering the interests of our own industries, but in advancing the cause of civilisation the world over. That the ever-increasing developments of chemistry should have been so directed as to have caused such world-wide havoc is greatly to be deplored, and it is to be hoped that the effects produced and the lessons learned will have throughout the ages the effect of teaching future generations the folly of diverting our beloved science from the arts of peace to those of war.

But to revert to my theme. The formation of the numerous bodies and associations, which I have referred to, has increased the volume of analytical work largely, and to that extent it is a good thing for the profession generally, but as the effect, so far as the commercial side of our work is concerned, is to increase the number of analyses of a similar nature there is a tendency to render a good deal of our work tedious and to some extent monotonous. In the nature of things such a result is almost inevitable, as with greater proficiency and greater experience in any particular direction the confidence of one's clients in one's work is sure to grow and, snowball-like, the volume of work is sure to increase, and thus the routine of the laboratory is too apt to assume the functions of something approaching a factory rather than the purely investigational work which we usually associate with a scientific laboratory.

In this respect, however, we are not far removed from the specialists in medicine or surgery who, after along preliminary training, find themselves in the hey-day of their prosperity dealing with special cases day in and day out.

There is, of course, in addition to the purely routine side of a practice, a considerable amount of work of a highly technical and exceedingly interesting nature which breaks the monotony of life and gives a zest to one's daily occupations.

The point which I am aiming to make clear is that, although the tendency of the age is to make specialists of us all, care must be taken to found that specialisation upon a sound scientific basis, and to avoid drifting into mere machines in controlling a limited section of trade or industry. Up to the present the policy of the trade associations has been almost universally to entrust the analytical work to trained chemists who have won the confidence of the public; and I think it will be a bad day for the trades concerned and for our profession if, as has been proposed in some cases and adopted in others, analysts are appointed at fixed salaries, or inadequate fees, to undertake the work of the associations I have referred to.

The question of professional fees, and the remuneration of chemists in general, is a somewhat complicated one, and there does not seem to be any way in which one or the other can be standardised. With regard to the fees charged by practising analysts, I think it will be generally agreed that before the war the charges made, even by leading men, were in many directions quite inadequate. This was partly due to a keen competition amongst chemists for what little outside analytical work was required in the earlier days, when the analyses were required for private information or control purposes. In some cases the fees were cut by men who had been inadequately trained, but as often no very great degree of accuracy was required, and very little opportunity was afforded of checking the results, there was no elimination of the least capable, and the competition of these with the better-trained men kept fees at a low level. In this way in many branches of work fees became more or less fixed, and by a general understanding they had to be accepted, especially by the younger members of the profession. Once fixed for any particular analysis it was very difficult for the individual to raise the fees without the risk of losing the work altogether. Thus it happened, in my case at all events, that a very considerable part of my practice was carried on at very little profit to myself.

With the altered conditions brought about as the result of the war it became imperative that a revision of fees should be made, and even the most altruistic of us were compelled by the force of necessity to raise our fees. The Institute of Chemistry made inquiry into the matter, and in the February number of the *Journal and Proceedings of the Institute* for 1920, stated that, as the result of their investigations, "the Council are of opinion that Fellows and Associates are justified in making a corresponding increase in their fees for professional services." Although unable to recommend any definite rate of increase over pre-war rates, the Council of the Institute state that an increase of 50 per cent cannot be regarded as excessive, while some practitioners have doubled their fees. This practically is the attitude which I myself have taken, readjusting the fees according to the work involved, but it is a matter of doubt whether the increases made in the fees cover the extra costs involved under present conditions.

With regard to chemists employed in whole-time engagements, I am afraid that in many instances the increases in remuneration have not been commensurate with the enhanced value of their services and the extra cost of living; but it is to be hoped that with the efflux of time and the stabilisation of the exchanges, the burdens at present borne will gradually be removed, and adjustments made which will remedy the present hardships.

During the past year your Council has worked assiduously, and, under the able guidance of our Secretaries, has kept the business of the Society and the interests of its members constantly in review.

One Committee, consisting of Messrs. L. Archbutt, W. J. A. Butterfield, G. Nevill Huntley, and G. Rudd Thompson, appointed by the Council to consider the desirability of making provision for supplies of standard chemical substances, has transmitted to the Council of the Institute of Chemistry a Report, a summary of which appeared in the September number of the *Analyst*.

The Committee is satisfied that there is a demand for Analytical Control Standards, at present being chiefly met by private enterprise and by the importation of the U.S.A. Bureau of Standards Samples, and that the demand appears reasonable for checking and educational, rather than commercial purposes.

The Committee recommend that the Society of Public Analysts should take the initiative in forming a representative Analytical Standards Committee, and the Council of the Institute of Chemistry have concurred with that recommendation, and have nominated Mr. F. H. Carr, Dr. J. T. Dunn, Mr. Lewis Eynon, and Mr. F. W. Harbord to act as its representatives.

That standards such as have been prepared or proposed would prove a great service, especially for educational purposes, scarcely admits of a doubt, but when it is suggested that these standards should be analysed side by side with commercial samples submitted for analysis, and that the fact should be stated on the certificate, I am very clearly of opinion that such use would be detrimental to the profession, and damage its prestige. In most cases the materials for which standards would be prepared would be commercial products, the analyses of which are almost invariably placed in the hands of experts, who are past-masters in the particular branch of analysis. To make any such statement such as that suggested would be tantamount to an admission of incompetency.

And now, in conclusion, I have to express to our indefatigable and ever courteous Secretaries, Mr. P. A. Ellis Richards, and Mr. E. Richards Bolton, the deep debt of gratitude under which I have been placed by their many kindnesses and invaluable promptings, both with regard to procedure and policy, during the year now coming to an end.

## BOOKS RECEIVED.

"A Dictionary of Applied Chemistry." By Sir EDWARD THORPE, C.B., LL.D., F.R.S. Vol. 1. Revised and enlarged edition A. to Calcium. 752 Pages. London: Longmans Green & Co. Price 60s. net.

"An Introduction to Zoology for Medical Students." By C. H. O'Donoghue, D.Sc., F.Z.S. 501 Pages. London: G. Bell & Sons. Price 16s net.

"Applied Colloid Chemistry: General Theory." By W. D. BANCROFT. 345 Pages. London: McGraw-Hill Publishing Co. Price 18s. net.

"Creative Chemistry: Descriptive of Recent Achievements in the Chemical Industries." By EDWARD E. HOSSON, M.S., Ph.D. With many Illustrations. 311 Pages. London: London University Press, Ltd. Price 12s. 6d. net

"Volumetric Analysis for Students of Pharmaceutical and General Chemistry." By CHARLES H. HAMPSHIRE, B.Sc., F.I.C. Third Edition. London: J. & A. Churchill. Price 7s. 6d. net.

"Physical and Chemical Constants and Some Mathematical Functions." By G. U. C. KAYE and T. H. LABY. Fourth Edition. London: Longmans Green & Co. Price 14s. net.

"The Chemistry of Synthetic Drugs." By PERCY MAY, D.Sc. (Lond.), F.I.C. Third Edition. 248 Pages. London: Longmans Green & Co. Price 12s. net.

## NOTES.

ROYAL INSTITUTION.—On Tuesday next, April 5, at 3 o'clock, Prof. R. A. Sampson, Astronomer Royal for Scotland, delivers the first of two lectures at the Royal Institution on (1) "Present Position of the Nebular Hypothesis"; (2) "Measurement of Starlight." The Tyndall lectures will be delivered by Mr. C. T. R. Wilson on "Thunderstorms," beginning on Thursday, April 7; and on Saturday, April 9, Dr. H. H. Dale begins a course of two lectures on "Poisons and Antidotes." The Friday evening Discourse on April 8 will be delivered by Dr. R. H. A. Plimmer on "Quality of Protein in Nutrition," and on April 15 by Mr. Ernest Law on "Wolsey as a War Minister."

GENERAL DISCUSSION ON FAILURE OF METALS.—A general discussion on Failure of Metals will be held on Wednesday, April 6, 1921, under the conjoint auspices of the Iron and Steel Institute, the Institution of Mechanical Engineers, the Faraday Society and the Institute of Metals, at the Institution of Mechanical Engineers, Storey's Gate, Westminster. There will be three sessions, commencing at 3 p.m., 5 p.m., and 8 p.m. respectively, with intervals for tea and dinner. Arrangements are being made to enable those attending to dine together at 6.45 p.m., at the Victoria Mansions Restaurant, 24, Victoria Street. Prof. Alfred W. Porter, D.Sc., F.R.S., President of the Faraday Society, will preside at the first session, when an introductory address will be delivered by Dr. W. Rosenhain, F.R.S., after which the Chair will be taken by Captain H. Riall Sankey, C.B., President of the Institution of Mechanical Engineers. Dr. J. E. Stead, F.R.S., President of the Iron and Steel Institute, will preside at the second session, and Eng. Vice-Admiral Sir George Goodwin, President of the Institute of Metals, will preside at the third session.. At each of these sessions a selection of papers will be submitted.

POSSIBILITIES OF POWER PRODUCTION.—Prof. Burstall, Dean of Science at the University of Birmingham, and head of the mechanical engineering department, addressed the members of the Institute of Electrical Engineers on the "Possibilities of Power Production," at the University on March 17. The present period might determine, said Prof. Burstall, what he called the "carbon period," and the sources of power derived

from the combustion of carbon in the shape of coal and oil. The two latter were a sort of capital, upon which mankind would continue to live probably for the next 250 years, but the time would come when they would have to seek other sources of power. He thought it probable, however, that future generations would not want the great amount of mechanical power that we considered to be indispensable, and might deprive themselves of it quite voluntarily in favour of other methods. Regarding the possibilities of steam engines, he thought that in the next 50 years they might look to obtaining a horse-power hour for an expenditure of about 8lb. of coal, beyond which it was extremely unlikely that the thermodynamics of the steam engine would allow them to go. So far as they could see, the power generated by coal or oil would be sufficient for present conditions, but it was as well to look for possible new sources of power energy. The resources of cold water power were distinctly limited, and would not satisfy anything like the whole of the wants of mankind. That the power of the tides would be used he had not the slightest doubt, but it had never appealed to him that the generation of power from water was going to do anything more than merely scratch at the needs that would be felt. The windmill would certainly be used extensively in the future. They had virtually only one other method of working, and that had been there since the birth of the human race—the sun. The problem was: How are we going to use this energy in the form we wanted it?

INSTITUTION OF PETROLEUM TECHNOLOGISTS.—The officers elected for the session 1921-22 are as follows. *President*—Prof. John Samuel Strafford Brame. *Past-Presidents*—Sir Boverton Redwood, Prof. Sir John Cadman, Sir Charles Greenway, Bart., Sir Frederick W. Black. *Vice-Presidents*—Herbert Barringer, Sir George Beilby, Sir John Cargill, Bart., The Rt. Hon. Viscount Cowdray of Cowdray, Arthur W. Eastlake, Sir Thomas H. Holland. *Council*—Alfred C. Adams, Herbert Allen, Major R. W. Barnett, M.P., Andrew Campbell, E. H. Cunningham Craig, Alexander Duckham, A. E Dunstan, James Kewley, W. R. Ormandy, T. C. Palmer, F. Mollwo Perkin, Robert Redwood, John S. Smith, Prof. W. W. Watts.

FRENCH GLASS INDUSTRY.—A company formed in Paris under the style of the Compagnie Industrielle des Verreries à Vitre, with a capital of 14,900,000 francs, is building large works at Cussett, in the Allier, which, states the *Journal Industrielle*, will be the most important in Europe for the manufacture of window-glass, by the Fourcalt process. The works are to be constructed on the site of the Cussett bottle works, which during the war were converted into steel works by the Acieries et Forges de Firminy. It is hoped that the works will be ready in October next. The Société Industrielle is stated to have a considerable interest in the new concern, which has absorbed the Verreries Valentin Mesiner at Saint-Etienne. The new company has also acquired the works at Aniche (Nord) belonging to the Société Industrielle de Verrerie, which were partially destroyed during the war, and subsequently rebuilt

## New Patents.

THIS List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

8604—Adam, W. G.—Production of amino-phenols, etc. March 19th.
8334—Ballantine, W. B.—Manufacture of ferrochrome alloys. March 17th.
8302—Barrett Co.—Manufacture of formaldehyde. March 16th.
8393—Carpmael, W—Manufacture of lithophones and barium hydroxide. March 17th.
8348—Green, R.—Compositions of cellulose acetate and nitrate. March 17th.
8515—Weight, O. W.—Manufacture of ammonium sulphate. March 18th.

*Specifications published this Week.*

136141—Carlsson, O. and Thall, E.—Methods of reducing the viscosity of viscous solutions of nitrous-cellulose and its compositions.
160114—Oswald, T. H. and Brown A. D. Dixon.—Apparatus for the extraction of oil from oleiferous sandstone shale or the like.

*Abstract Published this Week.*

*Thorium Salts.*—Mr. H. Wade of Hatton Garden, London, has recently been granted a Patent No. 156892 for an improved process of obtaining thorium salts A salt having the composition $TH(PO_3)_2 SO_4$ is obtained by heating at about 280°C. a solution of thorium sulphate to which has been added, phosphoric acid. After several hours the product separates as needle shaped crystals insoluble in water or dilute acid Alternatively thorium phosphate may be heated with sulphuric acid or, for a less pure product, a native thorium phosphate such as monazite may be used, the new product separating out while the rare earths do not.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

## MEETINGS FOR THE WEEK.

*Monday, April 4.*

Royal Institution, 4.30. (General Meeting).
Society of Chemical Industry, 8.

*Tuesday, April 5.*

Royal Institution, 3. "Present Position of the Nebular Hypothesis," by Prof. R. A. Sampson.
Royal Society of Arts, 4.30.

*Wednesday, April 6.*

Faraday Society and other Societies, 2.30, 5 and 8. Joint General Discussion on the "Failure of Metals under Internal and Prolonged Stress."
Royal Society of Arts, 8. "The Optophone," by Dr. Archibald Barr.
Society of Public Analysts, 8. "Detection and Estimation of Illipé Nut Fat used as a substitute for Cocoa Butter," by Francis G. H. Tate and John W. Pooley. "The Estimation of Strychnine in Scale Preparations containing Quinine and other Cinchona Alkaloids," by T. F. Harvey and S. Back. "A Colour Reaction for Aconite," by S. Mallaneh. "A Method for the Determination of the Acidity of Coloured Solutions," by J. L Lizius.

*Thursday, April 7.*

Royal Institution, 3. "Thunderstorms," by Dr. C. T. R. Wilson.
Chemical Society, 8.
Institution of Electrical Engineers, 6. "Some Recent Developments in Steam Turbine Practice," by K. Baumann.

*Friday, April 8.*

Royal Institution, 9. "Quality of Protein in Nutrition," by Dr. R. H. A. Plimmer.
Physical Society, 5.

*Saturday, April 9.*

Royal Institution, 3. "Poisons and Antidotes," by Dr H. H. Dale

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# A VOLUMETRIC METHOD FOR THE DETERMINATION OF LACTOSE BY ALKALINE POTASSIUM PERMANGANATE.*

By FELIPE T. ADRIANO.

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QUISUMBING (F. A. Quisumbing, "Determination of Glucose and Starch by the Alkaline Potassium Permanganate Method," *Philip. Journ. Sci.*, 1920, xvi., 581), of this laboratory, recently devised a volumetric method for the determination of glucose and starch by alkaline potassium permanganate solution, which is claimed to be shorter than and as accurate as any of the Fehling methods, either gravimetric or volumetric. It was thought worth while to apply this method to the determination of lactose in milk. For this purpose a lactose permanganate table similar to that for pure lactose for glucose and starch was prepared. Parallel determinations of lactose in milk were then made by the new, the Soxhlet, and the optical methods. The results show that for the determination of sugar in milk the new method, besides being more rapid, promises to be as accurate as either of the older methods, if not more so.

### *Previous Work on Milk Sugar Determination.*

So far as can be found in the available literature no quantitative method has ever been devised for the determination of lactose in milk by oxidation with potassium permanagante in alkaline solution. Greifenhagen, König, and Scholl (W. Greifenhagen, J. König, and A. Scholl, "Bestimmung der Kohlenhydrate durch Oxydation mittels Kaliumpermanganat in alkalischer Lösung," *Biochem. Zeitschr.*, 1911, xxxv., 177) determined the ration of lactose to the amount of oxygen used when the former is oxidised in an alkaline potassium permanganate solution, but they did not work out a method for the determination of this sugar in milk. Some determinations of lactose by the older methods are given here.

Woll (F. W. Woll, "Report on Dairy Products," *Bull. U.S. Dept. Agr., Bur. Chem.*, 1907, cv., 100) in his report on dairy products gives the following determinations of lactose in condensed milk:

| Analyst. | Lactose. By gravimetric method. Per cent | Lactose. By polariscope. Per cent |
|---|---|---|
| Jaffa and Stewart, California ... | 9·28 | 9·36 |
| Olson, Wisconsin ... ... ... | 9·91 | 9·19 |
| Jaffa and Stewart, California ... | 8·11 | 8·00 |
| Jaffa and Stewart, California ... | 10·87 | 10·74 |
| Jaffa and Stewart, California ... | 9·96 | 9·84 |

He called attention to the fact that the results obtained with the polariscopic method are, in all cases but one, lower than with the copper reduction gravimetric method. His observations were confirmed by the report of Patrick and Boyle (G. E. Patrick and M. Boyle, "Sub-report on Analysis of Dairy Products," *Bull. U.S. Dept. Agr., Bur. Chem.*, 1907, cv., 106), who, in their sub-report on analysis of dairy products, gave the following results:—

| Sample No. | Lactose By Soxhlet method. Per cent | Lactose By polariscope. Per cent |
|---|---|---|
| 2930 (Referee's sample) ... | 10·04 | 10·07 |
| 2530 ... ... ... ... ... ... ... | 10·51 | 10·19 |
| 2528 ... ... ... ... ... ... ... | 10·69 | 10·57 |
| 2610 ... ... ... ... ... ... | 10·15 | 9·97 |
| 2529 ... ... ... ... ... ... | 9·20 | 8·71 |
| 2531 ... ... ... ... ... ... ... | 9·37 | 9·00 |

Folin and McEllroy (O. Folin and W. S. McEllroy, "Copper Phosphate Mixtures as Sugar Reagents," *Journ. Biol. Chem.*, 1918, xxxiii., 513) have recently succeeded in introducing copper phosphate mixtures, the alkaline phosphate taking the place of tartrates, citrates, or glycerol in the analysis of sugars in urine, using a modified Benedict titration method. Folin and Denis (O. Folin and W. Denis, "The Determination of Lactose in Milk," *Journ. Biol. Chem.*, 1918, xxxiii., 521, 524) have applied this method to the determination of lactose in milk, and they claim that it gives accurate results. Their method as applied to milk is remarkably simple, for it does away with the preliminary preparation of protein-free filtrates, since albumin does not interfere with the titration, and it therefore "eliminates the cumbersome 'corrections' for the volume occupied by the protein-fat precipitates" In the same paper a picrate colorimetric method for lactose is described which is materially simpler than the one given by Dehn and Hartman (William M. Dehn and F. A. Hartman, "The Picrate Colorimetric Method for the Estimation of Carbohydrates," *Journ. Am. Chem. Soc.*, 1914, xxxii., 404). Parallel results obtained with the colorimetric method of Folin and Denis and the titration method are given to show that the latter is the more accurate.

### *Materials and Procedure.*

Quisumbing's Method as Applied to the Determination of Lactose in Milk.—Place in an Erlenmeyer flask 50 cubic cm. of 0·1 *N* potassium of permanganate solution, 25 cubic cm. of a solution of sodium carbonate containing 8·48 grms. of (anhydrous) sodium carbonate per litre, and 5 or 10 cubic cm. of the filtrate obtained as indicated below. Add sufficient water to make the final volume of the mixture 100 cubic cm. Heat the mixture on the heating device, consisting of an iron tripod with asbestos hood, with the heating power so regulated that its temperature is raised from 29° C. to 95° C. in two minutes, and continue heating for another two minutes after the temperature has reached 95° C. Remove the flask and add gradually 25 cubic cm. of 30 per cent sulphuric acid and 0·1 *N* oxalic acid solution until the liquid is clear. Titrate the excess of oxalic acid against standard 0·1 *N* potassium permanganate solution, adding the latter until the liquid assumes a pink colour that remains for a few seconds. The sum of the number of cubic cm. of 0·1 *N* potassium permanganate solution used in oxidation and in [illegible] minus the number of

* This investigation was undertaken at the suggestion and under the direction of Prof. M. L. Roxas. Published with the permission of the Director of the experiment station of the College of Agriculture, University of the Philippines.

cubic cm. of 0·1 *N* oxalic acid solution gives the number of cubic cm. of 0·1 *N* potassium permanganate solution that is actually used in oxidation The corresponding lactose value with the use of pure lactose is shown in Table II.

The pure lactose used in obtaining the data for this table was prepared as follows:—

To an alcoholic solution, saturated at 40° C. of chemically pure lactose obtained from a local dealer, absolute alcohol and ether were added, and the sugar was allowed to crystallise from the solution in a vacuum dessicator over sulphuric acid. When about half of the solvent had evaporated, the crystals were separated from the mother liquor by suction and then washed with small amounts of ether and absolute alcohol. The lactose was recrystallised three times in the manner described and the purified product dried for 16 hours at 40° C. under vacuum in an apparatus similar to that described by Browne (C. A. Browne, "Handbook of Sugar Analysis," London, 1912, 23). Its purity was determined as follows:

1·6450 grms. of the pure lactose were weighed and dissolved to 100 cubic cm. 25 cubic cm. of this solution were analysed by the Soxhlet method for the lactose content, and a portion was polarised after having been allowed to stand for 24 hours.

TABLE I.—*Determination of the Purity of Lactose*

| Method of analysis. | Lactose. Per cent. |
|---|---|
| Optical method | 100·00 |
| Soxhlet method | 99·98 |
| Average | 99·99 |

TABLE II.—*Determination of Lactose by the Alkaline Potassium Permanganate Method.*

| Lactose. mgs. | 0·1 *N* $KMnO_4$. cc. | Lactose mgs. | 0·1 *N* $KMnO_4$. cc. |
|---|---|---|---|
| 1 | 2·51 | 21 | 23·63 |
| 2 | 3·21 | 22 | 24·87 |
| 3 | 4·04 | 23 | 25·92 |
| 4 | 4·39 | 24 | 26·67 |
| 5 | 5·47 | 25 | 28·10 |
| 6 | 6·52 | 26 | 28·39 |
| 7 | 7·69 | 27 | 29·50 |
| 8 | 9·13 | 28 | 30·60 |
| 9 | 9·98 | 29 | 31·49 |
| 10 | 11·37 | 30 | 32·55 |
| 11 | 12·30 | 31 | 34·65 |
| 12 | 13·80 | 32 | 35·69 |
| 13 | 15·41 | 33 | 36·16 |
| 14 | 16·72 | 34 | 37·26 |
| 15 | 17·85 | 35 | 38·26 |
| 16 | 19·04 | 36 | 38·64 |
| 17 | 20·16 | 37 | 39·28 |
| 18 | 20·96 | 38 | 40·16 |
| 19 | 21·50 | 39 | 40·56 |
| 20 | 22·89 | 40 | 41·47 |

*Application of the New Method to the Analysis of Lactose in Milk.*

The milk under examination was analysed for its lactose content by means of the optical method, the gravimetric method, and the new method, thus making possible a comparison of the results of the three methods. That the milk samples should all be of equal concentration, the evaporated canned milk was diluted by mixing equal parts of the milk and water before proceeding with the analysis. To determine which of the methods is the most accurate, similar analyses were made on "synthetic" milk, prepared as indicated below. The preparation of the solution used for the gravimetric method and the new method is as follows (Report of the Committee on Editing Tentative and Official Methods of Analysis, *Journ. Assoc. of Official Agri. Chemists*, 1916, Bulletins 1 and 2, 87, 104, 289):—

Dilute 25 cubic cm. of milk of known weight with 400 cubic cm. of distilled water in a 500 cubic cm. graduated flask. Add 10 cubic cm. of the copper sulphate (dissolve 34,639 grms. of copper sulphate in 100 cubic cm. of water and dilute to 1 litre) solution and 8·8 cubic cm. of 0·5 sodium hydroxide, solution. After the addition of the alkali the mixture must still have an acid reaction and contain copper in solution. Fill the flask to the 500 cubic cm. mark; mix, filter through a dry filter, and determine the lactose in the filtrate, taking 50 cubic cm. for the copper reduction and 10 cubic cm. for the alkaline potassium permanganate method.

For the optical method the directions given in Sherman's "Organic Analysis," New York, 1912, 361, were followed.

The results of the analysis performed on canned and on fresh cows' milk are as follows:—

TABLE III.—*Determination of Lactose in Milk.*

(Figures express the percentages of lactose by weight.)

| No. | Sample. Description. | Lactose. Polariscope: Per cent | Lactose. Quisumbing's method. Per cent | Lactose. Soxhlet's method. Per cent |
|---|---|---|---|---|
| 1 | Sterilised Norway natural milk | 4·60 | 5·21 | 5·65 |
| 2 | Ditto | 4·56 | 5·20 | 5·64 |
| | Average | 4·580 | 5·205 | 5·645 |
| 3 | Sterilised evaporated milk | 6·12 | 9·52 | 9·76 |
| a4 | Ditto | 8·26 | 9·88 | 10·08 |
| a5 | Ditto | 7·28 | 9·70 | 9·88 |
| a6 | Ditto | 7·22 | 9·84 | 9·86 |
| | Average | 7·220 | 9·735 | 9·895 |
| 7 | Evaporated milk | 8·71 | 9·98 | 10·30 |
| 8 | Ditto | 8·78 | 9·99 | 10·24 |
| 9 | Ditto | 8·72 | 9·94 | 10·30 |
| 10 | Ditto | — | 9·94 | 10·29 |
| | Average | 8·736 | 9·962 | 10·282 |
| 11 | Sterilised natural milk | 4·41 | 4·50 | 4·52 |
| 12 | Ditto | 4·42 | 4·46 | 4·62 |
| 13 | Ditto | 4·38 | 4·53 | 4·46 |
| 14 | Ditto | 4·38 | 4·46 | 4·73 |
| | Average | 4·395 | 4·487 | 4·582 |
| 15 | Cows' milk from Los Baños | 4·50 | 4·80 | 5·08 |
| 16 | Ditto | 4·48 | 4·79 | 5·06 |
| | Average | 4·490 | 4·795 | 5·070 |

a. These samples were taken from the same can as No. 3, but they were treated with varying amounts of pure lactose. The percentage of lactose added was subtracted to find the true percentage of lactose in the milk.

*Analysis of Synthetic Milk.*

For the purpose of determining which of the three methods will give the most accurate results, analyses were made of "synthetic" milk, which was prepared in the laboratory by mixing:—

| | Per cent |
|---|---|
| Water ... | 87·75 |
| Fat (in the form of butter) ... | 3·40 |
| Protein (in the form of casein) ... | 3·50 |
| Pure Lactose ... | 4·60 |
| Mineral substances from the ash of canned milk ... | 0·75 |

The results are shown in Table IV.

TABLE IV.—*Analyses of Synthetic Milk.*

| Sample No. | Lactose. Polariscopic method. Per cent | Quisumbing's method. Per cent | Soxhlet's method. Per cent |
|---|---|---|---|
| 1 ... | 4·24 | 4·78 | 4·80 |
| 2 ... | 4·16 | 4·77 | 4·80 |
| Per cent of lactose added | 4·60 | 4·60 | 4·60 |

*Discussion of Results.*

Table II. gives the milligrms. of lactose corresponding to the number of cubic cm. of 0·1 $N$ potassium permanganate solution used in the determination as described. Table III. shows the results of the analysis of the different samples of milk by the three methods. Table IV. gives the results with synthetic milk with a known percentage of lactose. From these tables it may be seen that the percentage of milk sugar given by the optical method is consistently lower than by the Quisumbing or the Soxhlet method, and also that the Quisumbing method gave lower results than did the Soxhlet. The differences between the polariscopic method and the two oxidation methods are in most cases serious, whereas the oxidation methods may be considered to agree closely. The differences between the polariscopic method and the two oxidation methods are greater in the case of the sterilised evaporated milk than in that of the sterilised natural milk or the fresh cows' milk (see Table III.). It was thought that the differences might be due to changes in the sterilised evaporated milk that occur during manufacture but which do not occur in the sterilised natural milk or in the fresh cows' milk, and that such changes resulted in the formation of soluble products not precipitated by acid mercuric nitrate. The proteins or milk are most susceptible to hydrolysis during the process of evaporation, and would give rise to optically active products which may not be precipitated by mercuric nitrate. To test this point, the filtrates from samples 7 to 10, 11 to 14, and 15 and 16 (Table III.) were analysed for their nitrogen content by the Kjeldahl Gunning Arnold method (Report of the Committee on Editing Tentative and Official Methods of Analysis, *Journ. Assoc. of Official Chem.*, 1916, Bulletins 1 and 2, 87, 104, 289), with the following results:—

TABLE V.—*Nitrogen Determination of Filtrates from Samples 7 to* 10, 11 *to* 14, 15 *and* 16 (*Table III.*).

| Source of sample. | Nitrogen in samples— 7 to 10 Per cent | 11 to 14 Per cent | 15 and 16 Per cent |
|---|---|---|---|
| Filtrate for the polariscopic method ... | 0·0110 | 0·0130 | 0·0021 |
| Calculated as mgrms. alanin in 100 cubic cm. of filtrate ... | 70·00 | 82·50 | 12·70 |
| Filtrate for the reduction methods ... | 0·0006 | 0·0056 | 0·0016 |

These results show that hydrolysis of the protein occurs in the process of evaporation and sterilisation of milk. Thus the fresh cows' milk gives less nitrogen in the filtrate than either the evaporated or the sterilised milk. The differences are clearly seen if the nitrogen is expressed in milligrms. of a dipeptid or an amino acid such as alanin. Of course, nothing is known of the nature of these nitrogenous compounds. But, judging from the results of the analysis of samples 7 to 10, where the average difference between the polariscopic method and the two oxidation methods is greater than 1 per cent, and of samples 11 to 14, where the optical and the oxidation methods agree to within 0·1 per cent—both giving almost the same percentage of nitrogen in the filtrate—these soluble products may influence the rotation of lactose in either direction. It is very likely that other factors have an influence on the specific rotation of this sugar. This seems to be indicated by the results with synthetic milk. The casein used in the preparation of the latter must have been completely reprecipitated together with the fat by the acid mercuric nitrate, since hydrolysis of the casein was hardly possible under the conditions of the experiments; and yet the results of the sugar analysis by the polariscopic method are much lower than by the oxidation methods. Of course, no definite conclusions can yet be drawn from the results of only one set of experiments, but there are some indications that the mercuric nitrate, the ash, or the nitric acid, or all three, affect also the specific rotation of lactose. The influence of the factors seems to be cumulative in the case of the evaporated milk and compensating in the case of the sterilised milk.

*Summary and Conclusions.*

The attempt to apply the alkaline potassium permanganate method to the determination of lactose in milk has met with success. This method has advantages over the older methods in rapidity and accuracy. Lactose determinations run with the new method give consistently lower results than with the Soxhlet method.

The results obtained by the polariscopic method are very unreliable, and cannot be used for accurate work, especially in the analysis of canned milk. Where a high degree of accuracy in the results is required, the Quisumbing or Soxhlet method should be given preference.—*Philippine Journal of Science*, August, 1920.

HEALTH WEEK IN 1921.—The Secretary of the Health Week Committee, appointed by the Royal Sanitary Institute, announces that H.M. the King and H.M. the Queen have again graciously accorded their patronage to "Health Week," which will be held this year during the month of October.

## OVERGROWTHS ON DIAMOND.*

By J. R. SUTTON.

(Continued from p. 149.)

Reasoning from the above results, the following conclusions, *venio rogatum*, would seem to be justifiable:—

Yellow ground contains more calcite than blue ground does.

Calcic carbonate in suspension, or solution, deposits itself readily in thin layers on a diamond surface, causing that surface to approximate to the consistency of the common minerals in the pulsator concentrates.

This deposit being more easily wetted than a bare diamond surface is, the surface tension in water is increased, and that in grease decreased accordingly. Hence the coated diamond behaves like an equal mass of limestone on the grease tables.

The above account is drawn with no material alteration from my report made at the time some years ago. This report had been put away and the details half forgotten, although the conclusions were alluded to in a recently-published paper. But during the last few months the results appear to have received some extraneous confirmation perhaps sufficiently important to warrant the publication of them. This latter development will now be briefly described.

Now it is to be noted that if calcite, or limestone, can be made to form a crust on a diamond by artificial means, it ought to do the same naturally, in propitious circumstances. So far as the Wesselton yellow-ground diamonds are concerned, since they do not always adhere readily to the grease tables, this would appear to have been proved, or at least made probable, by the experiments described above. But since calcite occurs in fair abundance in some specimens of blue ground, there ought to be cases here and there in which blue-ground diamonds had acquired a calcite coating. The chances would be, however, that even so it would not follow that the coating would survive the rough treatment of mining and winning to the end at the grease tables. Moreover, should it be a thick coating and completely enclose a diamond, and survive intact, the diamond would certainly be rejected by the grease tables like the superfluous concentrates; or, in case of dry sorting, probably rejected as a valueless piece of white mineral. The chances are, therefore, not altogether favourable for the detection of a diamond with a thick coating. Nevertheless, diamonds heavily coated with a more or less complete shell are occasionally found. They come mostly from the interesting Bultfontein Mine, doubtless partly because the prevailing striated surface of Bultfontein diamond holds the coating best, and partly because of the abundance of calcite there; but they are found occasionally at Wesselton and Dutoitspan.

A significant fact about these particular lime-coated diamonds from blue ground is that the coating is not aragonite. For when it is boiled with cobalt nitrate it remains uncoloured. It is evident, therefore, that the coating was acquired at a late stage in the history of the matrix, and at a low temperature.

* From the Transactions of the Royal Society of South Africa.

Equally significant is the fact that calcite is not found inside cracked diamonds from the Kimberley area. The filling material has been taken from the cracks of many diamonds on the De Beers sorting tables and in no case has it been calcite. Usually it appears to be apophyllite ("The Diamond Mines of South Africa," p. 507), and pectolite has been found. Hence it may reasonably be inferred that the cracking of the diamonds took place at a relatively early period, and that the cracks became filled with a zeolite, or something of that sort, before the calcite was introduced, or separated out, into the matrix (F. P. Mennell, "The Miner's Guide," 1909, p. 147; also P. A. Wagner, "The Diamond Fields of Southern Africa," 1914, p. 75). Which is yet another argument against the popular delusion that cleavages among diamonds are due to explosion after the diamonds are taken from their matrix.

Occasional Dutoitspan rounded yellow diamonds are reported which have failed to adhere to the grease tables. They carry no obvious foreign coating any more than the Wesselton yellow-ground diamonds did, but presumably they carry a coating even though it be indefinitely thin. And it may be surmised that they come from the vicinity of local accumulations of calcite in the pipe rock. One typical specimen that had been rejected by all three tables adhered to the grease quite normally after immersion in a weak acid.

It may be of interest to quote here some remarks made by Boutan in his great work "Le Diamant," 1886, p. 171. Speaking from actual experience of Kimberley as it was somewhere about 1884—i.e., at a time when the blue ground had been reached and was being worked, he says of the diamond:—

"Il se présente sous bien des états divers de cristallisation, de couleur et de grosseur; mais il est presque toujours envelloppé d'une mince pellicule calcaire, qu'on enlève avec les autres impuretés qui pourraient ternir sa surface en le laissant pendant quelque temps dans de l'acide azotique bouillant."

It is a curious statement to make, however, that diamonds fresh from the mine were almost always encased in a chalky envelope (G. F. Williams, p. 208: "All the crystals in the blue ground were encased in a smooth bed of the same material, which did not adhere to the diamonds, so that their lustre, when extracted, was quite bright or glassy."). Certainly diamonds have always been put into acid—mostly aqua regia earlier, though hydrofluoric nowadays—before being sorted for shipment to London; but, as one understood, rather to remove impurities from cracks than especially to clean their surfaces, though of course it would do that too. And yet one hesitates to question the word of so careful a writer as Boutan. Possibly the explanation of the difficulty is either that such diamonds as he had the opportunity of seeing were thus coated, or that he mistook the main purpose for which the acid was generally used. True or not, the copyists lost a chance in not repeating the statement and so passing it on by their unanimity to the realm of historical fact. It may be mentioned here that it is well known at the De Beers pulsator that diamonds which have been lying for many years in the blue ground on the depositing floors are very intractable on the grease tables. Probably the long-continued

weathering has set calcite free, either from the blue ground itself or from the limestone underlying the floors, to form an incrustation on the diamond.

A clean diamond is not readily wetted by ordinary rain or river water. If it be immersed in such water it will come out dry saving where droplets can cling to irregularities upon its surface, and even these are easily shaken off. A triangular flake of diamond whose edges are 12 mm., and whose thickness is 1·25 mm., will float indefinitely upon a still-water surface. If the same flake be placed edge downwards in the water whose depth is about 6 mm., the lower edge will rest at the bottom of the water, and the top corner will project slantwise through the surface, and remain so, provided that the surface is kept fairly quiet. This is the largest thin flake there has been the opportunity to try, though doubtless much larger ones would behave in the same way. Small diamonds of good geometrical form up to at least 0·1 carat each will float on water, even when it is gently agitated, like corks, partly because of the surface tension of the water, but chiefly because they are not readily wetted, whereas most common minerals of the same size will submerge at once.

A number of simple experiments have been made with the object of ascertaining whether the addition of freely soluble substances to water would modify the surface tension between diamond and water. Saturated solutions of the following compounds showed no appreciable difference: Alum, Epsom salts, sal ammoniac, common salt, saltpetre. Saturated solutions of the following increased the tension somewhat: Chloride of lime, borax, hyposulphite of soda. On the other hand, a solution of caustic soda wetted the diamond thoroughly. But of all the substances tried, carbonate of soda proved by far the most effective. A diamond (crystal or bort) dipped into a saturated solution of carbonate of soda comes out wet and dries with a thick deposit of the substance. Even here, however, the wetting tends to be to a certain extent selective. The deposit as a rule dries thicker on the faces of the octahedron than it does on the edges; and, by the same token, thicker on the edges of the rhombic dodecahedron than it does on the faces. Some octahedra dry with their faces thickly coated (saving where deep triangular indentations interfere) and their edges scarcely dimmed, and some dodecahedra dry with their edges sharply outlined in white. This result may arise from faulty manipulation, or it may have been accidental to the limited number of stones treated; but it is curious that the observer occasionally comes across a diamond naturally coated on its octahedron faces with a black adamantine incrustation, while its edges are so clear that the colourless interior can be seen through them. On the other hand, a bort incrustation favours the dodecahedron faces of Wesselton "black" (nearly opaque) diamond.

One other, minor, point: If a diamond be placed in a solution of carbonate of soda contained in a glass vessel, the soda, in spite of its affinity for the diamond, will crystallise out, as the water evaporates, by preference on the sides of the vessel above the water surface, while the diamond remains uncovered in the solution. But in a solution of cane-sugar crystallisation will begin on the diamond alone, and the latter after a time will appear as if enveloped in an extensive cloudy condensation. The reasons need not detain us.

*Coated Diamonds: Some Observations and Inferences.*

Diamonds with a black incrustation are common, especially at Wesselton. In the mines of the Kimberley area this incrustation is usually very thin, and under magnification is seen to consist of minute dull black specks, more or less uniformly streaked over a somewhat rough and pitted surface—so thin, indeed, as to make the diamond look slaty-grey by reflected light, and smoky-brown by transmitted light. Not improbably this coating is allied to the frequent black spots included in the body of spotted stones. Whether, so far as the Kimberley mines are concerned, it represents the remains of a thicker coating which has been lost either naturally or in the process of mining and winning is doubtful. Mr. P. Ross Frames, however, has obtained, at the Premier Mine, Pretoria, a small diamond from the midst of a lump of graphite, and at this mine diamonds with quite a thick, soft black coating are sometimes found (P. A. Wagner, "Note on Graphite-coated Diamonds from the Premier Mine," *Trans. Geol. Soc. S.A.*, 1914; also "The Diamond Fields of Southern Africa," p. 143). The black coatings of the Kimberley area diamonds may be amorphous or crystalline diamond, or even graphite like the Premier ones. It may be due to a temporary increase of temperature in past time. But a sufficiently great general increase of temperature is not very likely, if only for the fact that diamonds are found in intimate association with crystal garnet and coloured zircon. Of bort the same may be said; and quite recently a lump of stewartite containing numerous grains of almandine garnet was found at Bultfontein High temperatures would be expected to render the garnet vitreous and to blanch the zircon.

The black incrustation is more likely to be a late corrosive sort of deposit on the diamond, quite independent of the process of crystallisation and not defining its final phase. And this view is supported by a small broken lump found at Koffyfontein which at first sight resembles a fragment of coal, but on closer examination proves to be transparent diamond thickly encrusted with a very hard black adamantine coat. It cannot be denied that the fracture preceded the incrustation.

This Koffyfontein specimen, then, helps us to see that the black spots common in diamonds have not necessarily always been enclosed within rapidly and continuously crystallising diamonds; and still less are these same spots centres of crystallisation in a metastable medium, but rather are incrustations on temporarily quiescent diamond surfaces analogous to the lime coatings dealt with above. For, suppose some black incrustation to form spots on a diamond crystal, then a further stage of diamond crystallisation would determine the black spots as inclusions like other minerals, such as garnet, pyrites, &c., captured in the same way. And this no doubt explains the frequent colour effects in their vicinity revealed by the polariscope. Also it helps us to

see that Dutoitspan rounded yellow diamonds, which are much less subject to strain and are less spotted than most other kinds, were probably formed more rapidly in one continuous process.

Haüy, indeed, attributed the rounded form of some diamonds to rapid crystallisation :

"Mais la formation du diamant ayant été précipitée, les faces ont subi des arrondissemens, comme cela arrive par rapport à une multitude de minéraux" ("Traité de Minéralogie," 1801, iii., p. 290). (Antonio Magliabechi expressed the opinion that diamonds do not grow larger by lying in the earth, but that their magnitude and figure are assumed at once (*Phil. Trans.*, 1707, No. 311). Leuwenhoeck gives reasons for thinking differently (*ibid.*, 1709, No. 324). But crystallisation fast or slow, necessarily postulates a solvent).

Whole stones encrusted in precisely the same way are met with now and again in the mines of Griqualand West. More important still, encrusted stones have been proved to exist inside larger ones. A good and typical instance was a Dutoitspan fragment of about two carats consisting of about a third of a whole white rounded diamond. Portions had split away from the original whole stone along two octahedral planes of cleavage, showing near the middle of the edge where the cleavage planes met a heavily encrusted little stone of fair form, as depicted on an enlarged scale in the annexed Fig. I. The incrustation was at least as hard as ordinary diamond. Observed through what was left of the natural face the inside of the fragment appeared to be extensively blurred with large black blotches —an illusionary effect caused by refraction, for actually, saving for the encrusted inclusion, the specimen was quite without blemish. Soft graphite inclusions are plentiful enough in the holes so common in the cleavage surface of diamond.

Owing to the high refractive index and frequent rounded habit of diamond, the true outlines of black spot inclusions are not always easy to make out, but frequently they seem to be shapeless. Sometimes they are mere flakes. They occur either singly or in groups. Jagersfontein diamonds are noted for the dense and solid appearance of their large black spots. At the other end of the scale of size are the smoky-brown clouds— the danger-signals of sensational literature, giving warning of impending explosion!—clouds of tiny black discrete particles. One would like to understand how the internal black spots are aligned with respect to the space lattice, as to which there is a striking suggestion in the case of a coated Bultfontein "rounded octahedron," within which at a depth of about a millimetre (as determined roughly by the focussing distance) under one face were three separate constellations of tiny black spots all lying in one octahedral plane of cleavage (two observations of a similar kind made by Des Cloizeaux, and cited by Boutan). These constellations of spots were of additional interest because of the gorgeous chromatic display they gave under the polariscope, and also for their obvious relationship to the surface markings, for exactly over each constellation was a particularly well-defined indented triangle. Could the millimetre or so of the face have been cleared off, then without a doubt the new face would have had much the same sort of coated appearance as the existing natural face had.

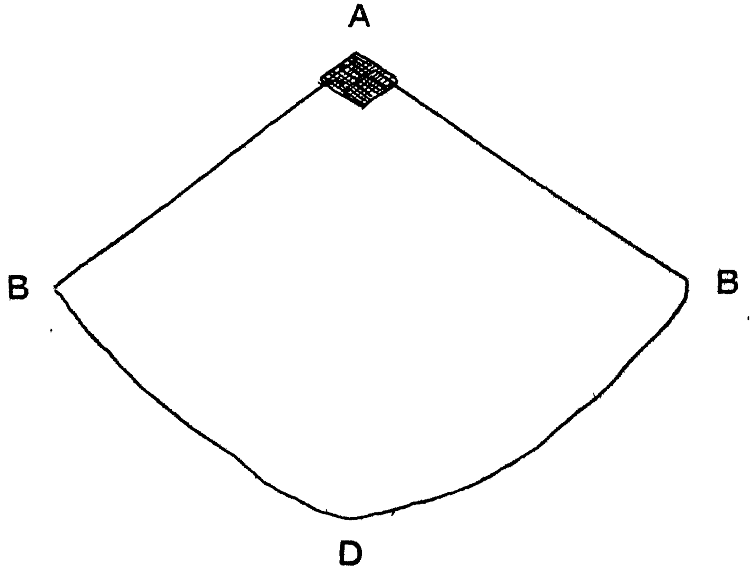


FIG. I.—Section of fragment showing position of inclusion.
A. Encrusted inclusion. AB. Cleavage faces. BDB. Natural surface.

(To be continued.)

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DIGITALIS LEAVES.—According to the physiological test, the activity of the digitalis leaf seems to decrease with age of the plant, differently to current opinion. Desiccation plays an important part, and a plant rapidly dried at 60° C. loses none of its activity (Ioachimoyla).—*Bull. Soc. Chim. de France*, January 20, 1921.

# SPIDERS USED IN MEDICINE.

By J. T. LLOYD, Ph.D.
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THAT insects and their by-products, such as shellac and honey, play an important part in the economy of man, is known to all. Perhaps, however, it is better known to the physician than to the layman, that a few spiders play their role in the practice of medicine. These spider remedies, like the insect medicines, are not of modern origin. In old works one finds frequent references to cobweb, which was then administered in the form of pills instead of the modern alcoholic pharmaceutical preparation, Tela Araneæ.

In the popular mind there is often little knowledge of the distinctions between spiders and insects, although the class *Arachnida* (to which the spiders, but not the insects, belong) contains several orders, such as the scorpions, that are closer akin to the spiders than are the insects Most of these are so distinct in superficial appearance that there is little probability of their being mistaken for spiders.

If one will remember that spiders have four pairs of legs, apparently no antennæ, and that their head is not separated from the thorax by a neck-like constriction, there need be no trouble to distinguish them from insects; which have three pairs of articulated legs, one pair of antennæ, and head and thorax separated by a distinct "neck." In the class Arachnida, spiders may be easily separated from other orders by remembering that thorax and abdomen are separated by a short, slender stalk, and the abdomen is not segmented. In their nearest relatives, the mites, the thorax and abdomen are fused and sack-like.

Since very early times many people have looked upon spiders with unfounded dread and superstition. During the medieval period, "Tarantism," a contagious disease that was common in Southern Europe, especially Italy, was believed to have been started by the bite of a spider. The victims of this disease were possessed with an uncontrollable desire to dance. In our own day and among our own people it is not unusual to blame the bite of a spider for swellings or itchings of unknown origin, but when questioned the sufferer is invariably unable to give other evidence that a spider is responsible for the trouble, than the usual answer, "What else could have done it?" On this negative evidence the blame is fixed for about 100 per cent of the "spider bites" of our people.

With the possible exception of a single species in our Southern States (*Lactrodectus mactans*, a jet-black spider with markings of yellow or red), and the true tarantulas of the South-West, it seems safe to accept that there are no spiders in our country whose bite need be in any way feared. The writer has handled large numbers of our native spiders, as well as (during excursions in the tropics) hundreds of the "banana tarantulas," which are not true tarantulas, but harmless spiders of a different family. True tarantulas may sometimes, however, be found in banana bunches. In no case has the writer been bitten, and frequent attempts to induce spiders to bite the tender skin between his fingers resulted in failure. Others who have made this experiment with success report that the wound inflicted is no more painful than a slight prick with a needle. That spiders do inject a virus into their victims is indisputable, but it is in quantities sufficient only to paralyse an insect. Besides, is is injected so slowly that little if any, could be secreted during the short interval that the "jaws" remain in the wound of an animal as large as man.

*Spider Web.*—All species of spiders are capable of spinning web, though far from all spin orbs or sheet-like webs for entrapping prey. Many species only throw out a "drag line" as they move from place to place, or drop from surface to surface and never spin a more complex web, except in wrapping their egg masses.

The web material, or silk, is produced in large glands within the spider's abdominal cavity. In the glands the material is liquid or mucilaginous but (except certain parts of the viscid silk) immediately hardens on exposure to the air. From the glands it passes to the exterior through silk ducts, which often open on movable, finger-shaped "spinneretts."

In all, spiders produce seven distinct kinds of silk; some thread-like, some band-like, some viscid, some dry. Though most spiders secrete more than one kind of silk, and some spiders secrete several kinds, no one spider secretes all seven. Each kind of silk originates in its own distinct glands and passes to the exterior through its own opening. (A careful and interesting account, written in non-technical language, of the habits, anatomy, and classification of spiders, may be found in "The Spider Book," by John Henry Comstock . Doubleday, Page & Co., 1912).

For pharmaceutical preparations an attempt is made to collect the sheet-like webs of *Cora. medicinalis* (*Tegenaria medicinalis*) from the corners of rooms in warehouses and kindred places. It is probable, however, that the webs of the several species of dwelling-inhabiting spiders enter into all pharmaceutical preparations of web No collector of webs could be expected to possess technical knowledge sufficient to enable him to distinguish species. If he should possess the required knowledge, it would be impracticable for him to take the time to apply his training for the examination of each web collected. Nor is there need for such discrimination. No reason why the web of one species of dwelling-inhabiting spider should be of different therapeutical qualities from another, has ever been recorded.

We do not know that a chemical analysis of spider web has ever been made. Tests given pharmaceutical preparations, however, show an absence of sugar, but give a slight reaction to Mayer's test for alkaloid. This is true also of tincture we have prepared from fresh web. The therapeutic value of the preparation may be in part due to this alkaloid.

In the present-day practice of medicine the large spiders of the sub-family *Aviculariinæ*, commonly known as "tarantulas," or "bird spiders," are employed by Homœopathic physicians. Under the name of *Mygale lasidora* the Pharmacopœia of the American Institute of Homœopathy, 1897, p. 408 gives directions for preparing the tincture of the "whole spider." Other references to the preparation and use of Mygale (tarantula) are given in Allen's "Encyclopedia of Pure Materia Medica," 1877, vol. vi., and elsewhere.

*Spider and Spider Web in Medicine.*—At least since the time of Pliny (first century A.D.) literature on medicine abounds in references to the use of spiders and their webs. The ideas of most of the old authors concerning the medicinal use of spiders, as may be noted in the following quotations, seem little more than "charm medicine" or superstition. Let us quote:

Spiders. "The fly-catching spider, wrapt in a linen cloth and hanged on the left arm, is good to drive away a Quotidian, saith *Trallianus* (sixth century, A.D.). But better if any of them be boiled with oil of bay to the consistence of a liniment; if you anoint the arteries of the wrists, the arms and temples before the fit, the fever abates and seldom comes again. *Koronides or Koranus* (King of Persia, who wrote a work on natural history). A spider bruised with a plaister and spread on a cloth and applied to the temples, cures a tertian. *Dioscorides* (first or second century, A.D.). The spider called Lycos, put in a quill, and hanged on the breast doth the same. *Pliny* (first century, A.D.). That house spider that spins a thick fine and white web, shut up in a piece of leather or a nut-shell, and hanged to the arm or neck, is thought to drive away the fits of a quartane. *Dioscorides* saith he proved it to be true. Three living spiders put into oil, let them presently boil on the fire, drop some of that oil warm into the ear that is in pain, and it profits much. Or press out the juice of spiders with juice of roses, and put it in with wool. *Marcellus Empiricus* (380-408, A.D., or later). Pliny bids infuse them in vinegar or oil of roses and stamp them and then drop some into the ear with saffron, and it will still the pain certainly: Dioscorides affirms as much. *Sofratus* . . . saith, that Cranacolapsus (a certain spider) drowned in oil, is a present remedy against poisons, as the Scholiast of Nicander (second century, B.C.) professeth. Aetius (about 500 A.D.) for suffocation of the mothers, applied a cerate of spider to the navel, and said it did great good."

Spider Web. "The spider's web is put into the unguent against Tetters, and applied to the swellings of the fundament, it consumes them without pain. *Marcellus Empiricus.* Pliny saith it cures runnings of the eyes, and laid on with oil, heals up wounds in the joints. Some rather use the ashes of the webs with Polonia and wine. Our chirurgians (surgeons) cure warts thus: They wrap a spider's ordinary web into the fashion of a ball, and laying it on the wart, they set it on fire, and so let it burn to ashes, by this means the wart is rooted out by the roots, and will never grow again. Marcellus Empiricus was wont to use the web of spiders found in the Cypress tree in a remedy for the Gout to ease the pains."—Mouffet, "The Theater of Insects," 1858, p. 1023.

A few of the early writers, like Antoninus Pius, and more during the medieval period, used the web to stop the flow of blood. For this purpose it was also used by the American Indians, as well as in domestic practice, no doubt with a real value. For example:

"Antoninus Pius (86-161, A.D.) was wont to say, that the quirks of sophistry were like to Spiders' Webs, that had a great deal of art and ingenuity in them, but very little profit. But how often hath the blood run forth from the body most miserably by a fresh wound? Yet it had been easy to have stopped it by laying on a spider's web."—Mouffet, "The Theater of Insects."

"*Telia Aranearum*, Cobweb. Everyone knows what this is, and how produced. It appears not in medicinal prescriptions, but as accident, for want of other helps, has taught its use to common people for stopping blood in a fresh wound. And this it seems to do by its extraordinary fineness; which makes it adhere to, and top up the mouths of the vessels, so as to prevent the effusion of their contents."—Quincy's Compleat English Dispensatory, 1749.

"*Aranearum Telae Pharm. Edinb.*, Cobwebs.—These are applied by the common people for stopping the bleeding of wounds; which the effect, not by any styptic power, but by adhering to the part, and closing the orifices of the vessels."—Lewis' Materia Medica, London, 1768.

"The web astringes and conglutinates, and is, therefore, vulnerary; restrains bleedings, and prevents inflammation. The country people have a tradition, that a small quantity of spider's web, given about an hour before the fit of an ague, and repeated immediately before it, is effectual in curing troublesome, and sometimes obstinate distemper. This remedy is not confined to our own country, for I am well informed that the Indians about North Carolina have great dependence on this remedy for agues, to which they are much subject; and I am acquainted with a gentleman long resident in those parts, who assures me he was himself cured by it of that distemper. And, indeed, experience confirms the efficacy of this medicine in the cure of agues."—James, "New English Dispensatory, London, 1747.

In May, 1809, the *Medical and Physical Journal* of London published a long article by Dr. Robert Jackson, calling to the attention of the profession the medicinal use of spider web, or cobweb, in the treatment of intermitting fevers. Frequent references have been made to this article by subsequent publications in Europe and in America. After Dr. Jackson's publication, the use of spider web in the treatment of malarial fevers seems to have been neglected until about 1865, when articles by Dr. L. M. Jones appeared in the *Lancet and Observer*, Cincinnati, and in Jones and Scudder's "Materia Medica." These again brought it to the attention of physicians:

"In asthma it is said to allay irritation, tranquilise the system, and act like a charm. In spasmodic complaints of females; in chronic hysteria, and other diseases attended with morbid irritability of the nervous system, it has been advantageously employed. Dr. Webster, of Boston, has found it beneficial in rheumatic affections of the head, asthma, and chronic coughs. He says it produces a pleasant delirium and exhilarating effects resembling the nitrous oxide gas. Dr. Gillespie used it in obstinate intermittents successfully, after other remedies had proved ineffectual. He thinks it more effectual than bark, arsenic, or any other remedy he has employed.

Dose.—Gr. v to vj, in pill; repeat every three or four hours. Dr. Jackson thinks a dose of gr. v produces nearly the same effects as one of gr. xx."—Jones and Scudder's "Materia Medica."

After the articles by Dr. Jones, the use of web gained constantly in the favour of many physicians. Present-day literature contains numerous testimonials to its use in the treatment of inter-

mittent fever, and in diseases of sudden appearance, when there is a tendency to congestion, with cool clammy skin; cool extremities, and cold perspiration.

Among the patients of the late Dr. L. A. Perce, of Long Beach, California, were many tourists afflicted with malaria. Some of these had been. to use his words, "dosed with quinine until it had lost its effect." For such patients he states that he employed tincture of "Tela Araneæ,' with gratifying results.

Until comparatively recently, as already stated, the web was administered in the form of pills, instead of in the alcoholic pharmaceutical preparation, "Tela Araneæ," of the present day.—*American Journal of Pharmacy,* January, 1921.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

*March* 17, 1921.

PROF. C. S. SHERRINGTON, President, in the Chair.

THE following papers were read:—

*"The Colour of the Light from the Night Sky."* By LORD RAYLEIGH, F.R.S.

To get information as to the chromatic character of the light from the sky at night, photographic exposures were made under coloured media selected for isolating various parts of the spectrum. By comparing the photographic densities obtained, it was concluded that the night sky was much yellower or less blue than the (clear) day sky. Comparison with direct sunlight or moonlight showed that the night sky was of the same quality as these.

Visual comparisons through coloured films showed that a blue film, which was equally bright with a yellow one against the night sky, was brighter against the twilight sky. These comparisons were not embarassed by colour differences, because the light was so faint as to give purely monochromatic vision. The two films matched one another equally well, whether they were seen against the Milky Way or against other parts of the sky. In the photographic work no special attention was paid to this point, the exposures being made to a considerable area of sky around the zenith. The diurnal motion, of course, brought successive areas of the sky into action during the long exposures.

One theory of the light of the night sky attributes it to sunlight scattered by a very rare gaseous atmosphere, situated so high up as to be outside the earth's shadow. The present observations are contradictory of this theory, which would require the night sky to have the same colour as the day sky.

The requirements, as regards colour and polarisation of light, would be satisfied if we regarded it as coming from an unresolved background of stars. They would equally be satisfied if we regarded it as due to sunlight scattered by meteoric matter.

*"The Dissipation of Energy in Permanent Ocean Currents, with some Relations between Salinities. Temperatures, and Currents."* By R. O. STREET.

On the assumption of slow non-turbulent motion a formula for the mean rate of energy dissipation in permanent ocean currents is obtained, which when integrated over the whole of the oceans, gives a dissipation at the mean rate of approximately $3 \times 10^{18}$ ergs per second. Simple relations between the strength of the current and the salinity and the temperature of the water are also found; and it is shown that, even with the scanty data available, satisfactory estimates of the currents in mid-ocean can thus be made.

*"The Vacuum Arc Spectra of Sodium and Potassium."* By S. DATTA.

Definite improvements in the measures for the spectra of sodium and potassium have been obtained by the use of sodium and potassium vapour lamps as sources. The lamps were excited in the manner described by Lord Rayleigh in his Bakerian Lecture in 1919, and they gave extremely narrow bright lines, such that the term diffuse, as applied to one of the series, becomes a misnomer. With potassium, an interesting combination pair indicating satellites to the diffuse series has been observed. The presence of potassium in the sun has been established, and some additional sodium lines have been identified with solar lines.

*"Heats of Combustion and Formation of Nitro-compounds. Part I.—Benzene, Toluene, Phenol, and Methylaniline Series.* By W. E. GARNER and C. L. ABERNETHY.

The adaptation of aromatic nitro-compounds as explosives for military purposes has necessitated a close investigation of certain of their properties, of which sensitiveness of impact, stability, and power are the most important. These properties are, however, fundamentally related to the heats of formation and heats of combustion of the various compounds, and as but few systematic investigations had been made of these constants, a more complete study has been attempted.

In this paper, the heats of combustion of all the isomerides of the mono-, di-, and tri-nitro toluenes, and of the mono-, di-, and tri-nitro benzenes, together with a number of nitroderivatives of phenol and methylaniline, have been determined, and the heats of formation and nitration calculated therefrom. The heats of formation and nitration of the isomerides of the di- and trinitro toluenes and benzenes show considerable variation, the values tending to a minimum when the nitro-groups are adjacent to one another or to a methyl group. An empirical relationship has been established connecting the heats of formation and the orientation of the nitro groups, which holds approximately for these compounds.

The heats of formation in any series increase to a maximum value, with the introduction of the nitro groups, this maximum being reached in the toluene, phenol, and methylaniline series (when symmetrical substitution takes place) at the dinitro derivative. The introduction of the methyl group into benzene modifies only slightly the shape of the curves showing the heats of formation of the derivatives, but the hydroxyl or methylaniline group has a much greater effect. The

parallelism between these derivatives of phenol and methyl aniline is very marked.

The high heat of formation of picris acid, 63·3 cal/mol, as compared with that of tri-nitro toluene, 29·1 cal/mol, provides an explanation for the very similar heats which are liberated in the detonation of these substances. The lower oxygen content of tri-nitro toluene is counter-balanced by its lower heat of formation. For a similar reason the unsymmetrical isomerides, though less stable and more sensitive than the symmetrical forms, should be more powerful explosives.

*"The Catalytic Dehydrogenation of Alcohols."* By E. K. Rideal.

Application of the approximation formula of the Nernst heat theorem to the equilibria

$$C_2H_5OH \rightleftarrows CH_3CHO + H_2 \text{ and}$$
$$(CH_3)_2CHOH \rightleftarrows (CH_3)_2CO + H_2$$

indicates that the dissociation constants should vary extremely rapidly with the temperature. The variation of the constants with the temperature was determined experimentally by means of a constant volume gas thermometer containing reduced copper as catalytic material. The velocity of decomposition of the alcohol at the surface of the solid catalyst was found to be much more rapid than the reverse bimolecular reaction. Concordant values for the equilibrium constants at various temperatures could only be obtained at low pressures. At elevated pressures and at high temperatures various secondary reactions occur which appear to be irreversible under the experimental conditions.

In the case of ethyl alcohol the value of $K_p$ was found to vary from $6·44 \; 10^{-4}$ at 125° C. to 0·91 at 275° C.; for isopropyl alcohol the respective values were found to be $2·82 \; 10^{-3}$ and 12·00 respectively.

The value of $\Delta U_0$ for the dehydrogenation of ethyl alcohol was found to be 11,500 cal. per grm. molecule, whilst the value calculated from the mean of the published values of the heats of combustion was found to be 10,700 cal. For isopropyl alcohol $\Delta U_0$ was found to be 20,100 calories per grm. mol.

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## SOCIETY OF GLASS TECHNOLOGY.

The March meeting of the Society of Glass Technology was held in Newcastle-on-Tyne on Wednesday, March 16, 1921. In the forenoon, by the courtesy of the directors, a visit was paid to the works of Messrs. Lemington Glassworks, Ltd., Lemington-on-Tyne. The party was conveyed to and from Newcastle by char-a-bancs, also also kindly provided by the Directors. At Lemington, members were met by Mr. C. Wilson (Managing Director) and Mr. W. W. Warren, A.M.I.C.E., A.M.I.E.E. (General Manager) A most interesting time was spent watching the processes in the manufacture of electric lamp bulbs and of glass tubing. Of special interest were the Westlake machines. This is an American automatic bulb-blowing machine, capable of turning out 1000 bulbs per hour. The workmen call it the "Iron Man." As the hand process was also in operation close by, the contrast between the two methods was the more striking. Messrs. The General Electric Co., Ltd., London, are the proprietors of the Lemington Works, the bulbs being sent to London to be completed.

Prior to the afternoon meeting, members of the Society were the guests at luncheon of the directors of Messrs. Lemington Glassworks, Ltd. A most enjoyable time was spent Mr. C. Wilson presided, supported by Prof. W. E. S. Turner, Dr. Travers, Mr. W. W. Warren, and a number of local glass manufacturers. Replying to a vote of thanks proposed by Dr. M. W. Travers, Mr. C. Wilson observed that apart from Lemington, the British glassmaker had hardly produced a bulb worth the name. He believed there was a fine future before the trade if only glassmakers would realise that they could not continue to work by rule of thumb, but must adopt the most scientific methods. The trade was bound up in science, and glassmaking was becoming more and more an engineering problem. It was also necessary that the workmen should realise that the success of the trade depended upon them as much as upon the employer. Mr. W. W. Warren also spoke eulogising the Westlake machine. He said he and his staff were out to make their works as efficient as any on the Continent or in America He claimed that they had already gone a long way towards attaining that object.

Prior to the reading of the papers at the afternoon meeting, the Chairman, Dr. W. M. Travers, paid a tribute to the work of the late Lord Moulton. Just a few days before his death, Lord Moulton had agreed to preside at the Annual Dinner of the Society to be held at the Hotel Cecil, London, on the evening of Wednesday, April 20. It was resolved unanimously that the Society record on its Minutes its appreciation of the great services rendered to science by Lord Moulton, and a vote of condolence with his family was passed, the members standing to record their sympathy in silence.

The following papers were read:—

*"Note on the Corrosion of Fireclay Refractory Materials by Glassmaking Materials."* By Donald Turner, B.Sc.Tech., and Prof. W. E. S. Turner, D.Sc.

The research in question, said Prof. Turner, was an attempt to obtain information as to the relative attack of batch materials on fireclay refractories. The results were of much interest, and scarcely in keeping with some traditions. It was found that even at 800°, soda ash attacked fully-burnt fireclay, and particles of a certain size lost between 11 and 18 per cent of their weight in the space of three hours. Again, whereas soda ash was so corrosive, saltcake was not nearly so active, and in comparative tests took up no more than 1 per cent of the fireclay at 800°. The results indicated that the temperature of decomposition of the alkaline salts influenced their corrosiveness, those decomposing at lowest temperatures, such as nitrates, being most corrosive. The need of thorough batch mixing was also emphasised, as any segregation of the alkaline salt made it more likely that corrosion would occur.

*"The Clouding of Glass."* By M. W. Travers. D.Sc., F.R.S.

This research was intended to determine the causes of the clouding of soft soda glass during

lampworking operations a short distance from the hottest zone. He showed that when pure hydrogen and air were used there was no clouding effect, and hence came to the conclusion that some impurity in the gas was an important factor in causing clouding. Further experiments showed that sulphur dioxide when present in the gas in more than a very small proportion, was the chief factor in producing this effect. Theoretical considerations also pointed to the probability of sulphur compounds being the cause of clouding, and some figures obtained by using Nernst's heat equation agreed very closely with the results obtained experimentally. In one experiment, pure sulphur dioxide was passed through a tube heated by a bunsen flame. No fogging occurred until the tube had cooled.

The lecturer pointed out that the cure for the defect seemed to lie in the purification of the gas used. He referred to the work of Dr. C. Carpenter, of the South Metropolitan Gas Co., who passed the gas through an iron tube containing clay balls soaked in nickel salts. The reaction that followed was represented by the equation $CS_2 3H_2 = CH_4 H_2S$.

In the course of the discussion that followed, Mr. W. W. WARREN remarked that one of the difficulties encountered in the use of the Westlake machine was the effect of sulphur in the working pot. A white splotch was produced on the glass which made the bulb unusable.

Mr. F. F. S. BRYSON, Physicist to the Glass Research Association, said that that Association had also been considering the same problem, and had been in communication with Dr. Travers on the matter. He exhibited a number of lantern slides in which the effect in question was well shown. Mr. E. A. Coad-Pryor, Mr. Marden, and Prof. W. E. S. Turner also took part in the discussion of the papers.

Owing to lack of time, the last paper on the agenda, namely, "The Shrinkage, Porosity, and Density of British Fireclays after Firing at 1500°," by Edith M. Firth, B.Sc., and Prof. W. E. S. Turner, D.Sc., was postponed to another meeting.

## NOTES.

CATALYTIC DECOMPOSITION OF CHLORACETIC ACIDS.—Whereas catalysis gives cetones with acids, chlorinated cetones are not obtained with chlorinated acids.—Whether thorine, kaolin, or bone black be employed, the mixture HCl, CO, $CO_2$, and C, is produced with monochloracetic acid. With trichloracetic acid bone black gives, at 250° C., chloroform and $CO_2$, chloral did not give chloroform with CO, as might have been expected.—*Comptes Rendus*, January 17, 1921.

CHEAP MANURES FOR THE FARMER.—An important arrangement which will have considerable bearing upon prices and supplies of artificial manures next season has just been completed between the Phosphate Commissioners, in conjunction with the Ministry of Agriculture, and Mr. George V. Parker, acting on behalf of the South Wales Basic Slag Company, Ltd., which is closely allied with the well-known steel firms of Messrs. Baldwins, Ltd., and Messrs. W. Gilbertson & Co, Ltd. It will be remembered that the mandate for the administration of the Island of Nauru, formerly owned by Germany, was conferred upon the British Empire, an Act of Parliament was ultimately passed by which the United Kingdom was entitled to 42 per cent of the yearly output of phosphate produced in the island. Mr. George V. Parker has acquired the whole of this allocation of 42 per cent of the output of phosphate rock from Nauru. Although the purchase price is not stated, the amount involved constitutes by far the largest transaction which has taken place in the history of the British fertiliser industry, the previous largest deal having been in Florida phosphate rock, which was purchased by the British Government during the war. It is anticipated that some 180,000 tons of high-grade phosphate rock will be shipped during each year, and the material will be delivered to various ports here, from which it will be distributed throughout the United Kingdom. By arrangements with the Ministry of Agriculture, a proportion will be sold next season as basic phosphate, at under 3s. per unit of phosphate of lime, delivered to farmers' stations. As the present quotations of phosphate of lime range from about 5s. to 7s. 6d. per unit, it would seem that the Government pledge of cheap phosphatic manures for the farmer, as the outcome of the acquisition of Nauru Island, is at long last going to be kept. The first consignments of phosphate rock from Nauru are expected to arrive in this country in June and July, and already one-third of the next six months' production has been contracted for.

## New Patents.

THIS List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W.C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

### *Latest Patent Applications.*

6232—Angel, H. R.—Treatment and reduction of sulphide refractory, etc, ores. Feb. 24th.
6160—Carpmael, W.—Manufacture of ethylene derivatives. Feb. 23rd.
6313—Christenson, O. L.—Production of ammonium chloride in coking or distilling coal. Feb. 24th.
6446—Christenson, O. L.—Method of producing ammonium chloride. Feb 24th.
6521—Humphries, H. B. P.—Packing, etc., material for scrubbing and absorption towers, distilling columns, etc. Feb. 26th.
6036—Imray, O.—Manufacture of mordant dyeing dye stuffs and chromium compounds thereof. Feb. 22nd.

### *Specifications published this Week.*

158992—Kelly, A. A. and Jones, B. D.—Process for the preparation of alkali pentaborates direct from boron ores.
135854—Fleming, R.—Process for conversion of hydrocarbons into hydrocarbons of lower boiling point.
159054—Maass, O.—Process of separating aqueous and other vapours from liquids and solids for preparing dilute sulphuric acid.
159086—Sierun, S. E.—Process of producing oxide of aluminium from chloride of aluminium.

### *Abstract Published this Week.*

*Separating Mercury from Amalgam.*—Mr. S. H. Cocks of 6a, Ormonde Terrace, Regents Park, London, has recently obtained a Patent No. 152815 for an improved apparatus for separating mercury from amalgam, which comprises a chamber provided with a screwed air-tight cap, a perforated base secured to the chamber by a clamp, a filtering medium, such as canvas, overlying the base, and a valved pipe for introducing air or water under pressure.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

## MEETINGS FOR THE WEEK.

*Monday, April 11.*
Royal Society of Arts, 8.
Royal Institution, 4. (General Meeting).

*Tuesday, April 12.*
Royal Institution, 3. "The Measurement of Starlight" by Prof. R. A. Sampson.

*Wednesday, April 13.*
Royal Society of Arts, 4.30.

*Thursday, April 14.*
Royal Institution, 3. "Thunderstorms," by Dr. C. T. R. Wilson.
Institute of Chemistry. (At Liverpool).
Institution of Electrical Engineers, 6.
Optical Society, 7.30.

*Friday, April 15.*
Royal Institution, 9. "Wolsey as War Minister," by Ernest Law.

*Saturday, April 16.*
Royal Institution, 3. "Poisons and Antidotes," by Dr. H. H. Dale.

G. R.

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THE CHEMICAL NEWS.

VOL. CXXII., No. 3183.

## DISINTEGRATION OF ATOMS BY $\alpha$-PARTICLES.

By F. H. LORING.

THE following abstract should be of interest to readers of the CHEMICAL NEWS. In a recent communication to *Nature* (March 10, 1921, cvii., 41), Rutherford and Chadwick state: It had been found that the long-range particles were charged hydrogen atoms (CHEMICAL NEWS, cxviii., 311) which indicated that some of the nitrogen atoms were disintegrated by the $\alpha$-particles. Recent improvements in the optical conditions have been made, whereby the counting of the scintillations on the zinc-sulphide screen has been made easier, and the results now obtained are considered more reliable. They had been able to show definitely that the H-atoms from nitrogen have a greater range than those from hydrogen. The H-atoms driven from the hydrogen molecule or from a hydrogen compound have a maximum range of 29 cm. of air, while the H-atoms from nitrogen have a greater range of 40 cm., giving a ratio of 1 to 1·4. The range of the bombarding $\alpha$-particles in these experiments was 7 cm. "This result shows that these particles cannot possibly arise from any hydrogen contamination."

Other elements were subjected to the $\alpha$-particle bombardment with the result that *long-range* H-atoms were liberated from boron, sodium, fluorine, aluminium and phosphorus; but the number from boron and sodium was much fewer than from the other four elements. It had been found previously that the *long-range* H-particles were not liberated from either oxygen or carbon dioxide molecules.

With solids, the bombardment was against a thin film of the element or its oxide. Observations of the number of scintillations were made through a thickness of mica corresponding to a distance of 32 cm. of air, and the results are said to be independent of the presence of hydrogen or any hydrogen compound in the material.

The following elements were bombarded, and they showed very little, if any, effect with an absorption corresponding to 32 cm. of air:—Li, Be, C, O, Mg, Si, S, Cl, K, Ca, Ti, Mn, Fe, Cu, Sn and Au.

The gases $O_2$, $CO_2$ and $SO_2$ were examined for H-particles. At absorptions *less* than 32 cm. of air no traces of H-atoms were obtained. Elements other than the foregoing have not yet been examined for particles having a range less than 32 cm. in air.

The particles from all the first-mentioned elements have a maximum range of at least 40 cm. The particles from aluminium have a surprisingly long range of 80 cm.

While there is no experimental evidence of the nature of these particles, except in the case of nitrogen, it seems probable that they are all H-atoms liberated at different speeds. Assuming the law connecting the range and velocity of the H-particles to be the same as that for the $\alpha$-particles, it would appear that the energy of the H-particles from aluminium is about 25 per cent greater than the energy of the incident $\alpha$-particle.

Rutherford and Chadwick remark :"It is of interest to note that no effect is observed in 'pure' elements [those without isotopes, such as C, N, O and F] the atomic mass of which is given by $4n$, where $n$ is a whole number. The effect is, however, marked in many of the elements the mass of which is given by $4n+2$ or $4n+3$. Such a result is to be anticipated if atoms of the $4n$ type are built up of stable helium nuclei and those of the $4n+a$ type of helium and hydrogen nuclei.

"It should also be mentioned that no particles have so far been observed for any element of mass greater than 31. If this proves to be general, even for $\alpha$-particles of greater velocity than those of radium C, it may be an indication that the structure of the atomic nucleus undergoes some marked change at this point; for example, in the lighter atoms the hydrogen nuclei may be satellites of the main body of the nucleus, while in the heavier elements the hydrogen nuclei may form part of the interior structure"

The importance of this experimental work is of very far-reaching significance, especially in affording a powerful tool for investigating subatomic phenomena and revealing secrets which some years ago one would consider beyond the power of man to discover. The long-range particles from aluminium seem to show that we are on the track of setting free atomic energy on a larger scale than hitherto found possible.

Now that Aston has been able to isolate spectrographically some of the isotopes of the alkali metals by using a heated anode (*Nature*, March 17, 1921), we seem to be on the eve of clearing up one or two outstanding problems of chemistry and at the same time more definite knowledge of the atom itself is revealed. It would appear that lithium has isotopes of masses 6 and 7, potassium 39 and 41, rubidium 85 and 87. Sodium gives a single line answering to the atomic mass of 23. If no other mass is discovered sodium would then be known as a "pure" element.

In addition to the references given above, the following literature may be consulted: Rutherford, *Phil. Mag.*, June, 1919; *Proc. Roy. Soc.*, (Bakerian Lecture), 1920, xcvii, 374; Loring, CHEMICAL NEWS, 1920, cxx., 73, 181, 205; cxxi., 105. Aston's results in measuring the masses of isotopes are recorded in the foregoing papers by the present writer. See also CHEMICAL NEWS, 1920, cxxi., 315; cxxii., 8 ("*isotypes*" was a typographical error: it should read "*isotopes*").

THE INSTITUTE OF PHYSICS.—The Meeting to inaugurate the Institute of Physics will take place on Wednesday, April 27, 1921, at 6 p.m., in the Hall of the Institution of Civil Engineers, Great George St., Westminster. Sir Richard Glazebrook, K.C.B., President, will preside, and Sir J. J. Thomson, O.M., will deliver an Address. Mr. A. J. Balfour is expected to be present and extend a welcome to the Institute. Non-members of the Institute or of the Societies associated with it may obtain tickets of admission on application to the Secretary, 10, Essex Street, Strand, W.C.2.

## OVERGROWTHS ON DIAMOND.*

By J. R. SUTTON.

(Concluded from p. 162.)

I have observed the phenomenon of the superimposition of a deep indented triangle over a shallow-seated spot or spot area once or twice before, and thought that it could be explained as mere coincidence. The case of the above-mentioned Bultfontein stone nevertheless makes it pretty certain that spots may on occasion interrupt the orderly rate of crystallisation, and hence that they are not likely to be action centres of growth themselves.

It is quite on the cards that a competent study of the black incrustation and the black spots may yet explain a great deal that is yet unknown about the diamond macle and so justify the use of the name. For the majority of macles are spotted—some in the composition plane—as it is not quite accurately termed, seeing that the seam is not as a rule a plane at all—others in most remarkable streaks along the grain, and yet others in both ways together. The streaks running along the grain—*i.e.*, in the dodecahedral cleavage planes—are very common in macles, and practically non-existent in simple crystals. Some macles display, indeed, saving for a comparatively clear space in their centres, almost as much streak as diamond. Granting, for argument, that the streaks are graphite, they show at least that macles must have grown in a more graphitic environment than simple crystals did. It is not meant by this that the graphite must have forced the macling, for many macles are quite free from streaks and spots too, but that the two sorts of conditions were unlike under which macles and simple crystals came into being, conditions perhaps in which the production of graphite was more favourable than it was elsewhere. In this connection we may observe that the blue grounds of the Premier and Jagersfontein Mines are reported to yield a large percentage of macles and much graphite.

Falling within the category of coated diamonds, though not in the market sense, are the occasional irregular crystals upon whose surfaces thick coatings of a kind of grey bort have been deposited. This bort might to all appearance have been put on in the form of a wet paste, with a spatula, and then dried hard. Such specimens as have come to light have never been completely covered by the bort, although there are pieces of the bort which look as if they may have diamond within. This kind of bort overgrowth is not commonly found on a natural crystal face, but rather on what appear to be faces of arrested growth, say on surfaces of attachment, and may be material which has flowed into and filled the interstices between the diamonds of a cluster, at any rate it simulates that effect. A Dutoitspan flat diamond which was found recently had such a surface of attachment covered with bort, and on the surface of the bort, which was much pitted, there were numerous tiny black particles—whether of graphite or of amorphous black diamond could not be determined—filling the pits. The bort overgrowth here spoken of forms a link between common grey bort and the cement-like stuff of the next section, merging by insensible gradations from the one into the other.

*From the Transactions of the Royal Society of South Africa.

### *The Hailstone Structure.*

Unequivocal proof that the crystallisation of diamond is by no means necessarily a rapid and continuous process is supplied by the diamonds which in a previous paper have been likened to hailstones ("Some Controversial Notes on the Diamond," *Trans. R.S.S.A.*, 1920, viii., 129). Such diamonds are common enough, although they do not seem to have attracted much attention. Typically they consist of what looks like a kind of hardened and more or less porous paste, superficially not unlike Portland cement, alternating with layers or shells generally of curvilinear section of clouded crystal diamond. Sometimes the core is diamond; now and then it is diamond with a small central spot of some cognate material; often it is an irregular lump of cement alone so far as one can judge of its interior without breaking it open. When the outermost layer is cement, the specimen is shapeless; when it is diamond it tends to a diamond contour—cube, octahedron, or dodecahedron—and it is usually much cracked. Naturally it is only in the broken specimens that the structure is revealed. The condition of the specimens indicates a higher co-efficient of expansion for the cement than for diamond; unless the cement is subject to secular shrinkage, which on various grounds is not altogether improbable. The colour of the cement varies from light to dark dirty-grey. It is much softer than diamond, writing a light grey streak on black amorphous bort. The denser pieces have a somewhat higher specific gravity than pure diamond; a lower specific gravity suggests porosity. Like diamond, the cement is insoluble in acids.

On account of the theoretical importance of these hailstone-like overgrowths, I venture to attempt a description of some characteristic forms. The majority are from Bultfontein.

1. A broken piece showing an irregular core of light grey cement, surrounded by a thin shell of diamond, then a thin shell of cement, the whole enclosed in a thicker shell of diamond of irregular outline. Weight 4·5 carats.

2. An irregular lump showing no trace of crystal diamond. A crater-shaped hole in a projecting corner contains a tiny fragment of bright green mineral, probably chrome diopside. 0·5 carat.

3. A broken piece with a dark grey cement interior surrounded by a confused mixture of light grey cement and diamond. 0·7 carat.

4. A flat piece showing a centre of clouded crystal diamond surrounded by an inner ring of black crystalline diamond, and an outer ring of light grey cement. The original stone, of which this is a fragment, must have been roughly spherical. 0·5 carat.

5. A flat cleavage fragment showing a hexagonal flake of clouded and spotted diamond with an outer crystalline shell of a composition apparently intermediate between diamond and cement. This specimen is of further interest as showing dodecahedral cleavage with the dodecahedral striations. 1 carat.

6. A flat cleavage fragment in plan something like the section of a pear cut parallel to the stalk. This has a crystalline core, surrounded by cement,

then a thin crystalline shell, then a thicker shell of cement intersected by a portion of a very thin crystalline shell following the contour of the first for about a quarter of the way round its perimeter, and lastly, a crystalline casing. 0·2 carat.

7. A broken-off corner consisting of a black crystal interior surrounded by alternate shells of cement and diamond. Three more or less complete shells and four cement ones may be counted. 0·2 carat.

8. A flat fragment consisting of a crystal central portion surrounded by four concentric shells of about 0·5 mm. thick, two of light-coloured cement, and two of crystal. 3 carats.

9. A flat fragment broken from one end of what, to outside appearance, must once have looked like a cube of highly crystalline bort. A scraping of the broken face with a knife-blade indicates that it consists of numerous exceedingly thin successive overgrowths of bort and cement. 2 carats.

10. A somewhat hemispherical piece. The central crystal core is surrounded by no less than 17 alternate concentric rings of light grey cement and black crystal diamond. 0·4 carat.

11. A pyramid consisting of half of a "rounded octahedron." The edges, where dodecahedral striations would emerge on ordinary diamonds, are here of cement. Rather it looks like a piece of octahedral cement with projecting grey crystal bosses on the triangular faces, thus inclining the form to that of the plus and minus tetrahedral twin. 0·8 carat

12. An irregular lump of cement to outside appearance. When first seen it was pitted with small elongated holes as though it had been prodded with the point of a pen-knife. At the time of writing it is scored over much of its surface with deep meandering cracks which either are (and look like) shrinkage cracks, or were there all the time, but hidden by being filled up with cement which afterwards fell out. 2·7 carats

13. A fragment similar to No. 10, excepting that it has rather fewer shells, has an outer coat of shiny bort, and gives the impression that the fractured face showing the shells has been glazed over with a vitreous layer and polished. The outer contour is that of the cube carrying the usual well-defined square indentations. Unlike most hailstone forms, which cleave in the dodecahedral plane, the fractured face of this specimen lies in the octahedral plane. 0·5 carat.

Mr. J. Parry has kindly analysed two small diamonds carrying this cement crust. It was not possible to separate the diamond from the cement, consequently the specimens had to be treated entire. They gave only the familiar indication for iron, and a rather stronger one for magnesia. The actual proportions of these elements in the cement itself cannot, of course, be determined until a large enough sample can be procured separate. Meanwhile, it seems reasonable to infer that the comparative softness of the cement is due to the magnesia, seeing that a considerable admixture of iron with diamond (*e.g.*, stewartite) does not diminish the hardness at all.

*Laminated Diamonds.*

Laminated diamonds are very common. In one sense they appear to be examples of the general phenomena of overgrowths, and for that reason are included in this paper.

Suppose a model octahedron of glass to be split parallel to a pair of opposite faces into a number of thin laminæ; next the laminæ to be sealed together in their original positions by means of a transparent cement slightly harder (or slightly less solvent) than the glass; and lastly the edges of the octahedron to be abraded (or disolved) away. The layers of cement being more resistant than the glass will stand out in slight relief as the attack proceeds.

Next let the same octahedron of glass be split again into thin laminæ parallel to another pair of opposite faces and the ecmenting and abrading (or dissolving) process repeated. We shall obtain another set of layers protruding in relief and intersecting the first at a constant angle.

Finally, let the series of operations be repeated for laminæ parallel to the two other pairs of opposite faces. The whole octahedron will now be spaced out into a device of small octahedra, marking its faces with a network of flush interlacing equilateral triangles, showing in relief on the reduced edges.

Laminated diamonds are exactly like this. The laminæ are sometimes as thin as paper; more often they are in the vicinity of half-a-millimetre thick. They are not hemitropic. They alter the overall contour of a crystal very little, differing essentially in this respect from the macle, but on the other hand they modify the surface detail to some extent. The layers corresponding to the cement layers of the hypothetical glass model always protrude where they show themselves, and, as a rule, they may be easily felt with the fingernail or with the edge of a knife. A formal analogy will be found in the octahedral structure of iron meteorites, wherein kamacite stands for the glass, and the less easily dissolved taenite for the cement.

The laminæ scarcely ever manifest their existence save on the well-developed somewhat coarsely rilled faces of the rhombic dodecahedron or tetrahexadron. On octahedron faces they are rarely seen, as also on the finely-grained rounded edges of the octahedron (which are embryo dodecahedron and tetrahexadron faces). On octahedron-dodecahedron combinations they may be traced all round a stone excepting where the octahedron faces interrupt. The intersections of the laminæ with the octahedron faces, however, are often indicated by an array of indented triangles.

In the majority of cases only one set of parallel laminæ appear on any one diamond. When two sets appear, intersecting on a solution face, one set is nearly always much more prominent than the other. An examination of a great number of laminated specimens has only determined a very few—and some of these doubtful—with more than two sets of laminæ in one stone.

In Fig. II. I have attempted to depict a laminated octahedron-dodecahedron combination from Wesselton, showing two sets of laminæ. It is one of the rare cases in which the edges visibly cut the octahedron face. Though some relationship between the laminæ and the indented triangles is shown, it is not so marked as in many other specimens, wherein, while the edges themselves are not visible, their course is traced out by rows of little triangles, all much of a size, in a row.

On the rotating stage under the microscope, the edges of the laminæ give a singularly pleasing effect. They prove them to be more of the nature of steps down facing away from the shorter diagonals of the rhombic faces, than of definite protrusions; and their undeviating straightness, so different from the vacillating composition plane of the macle, contrasts sharply with the rippled surfaces they cut.

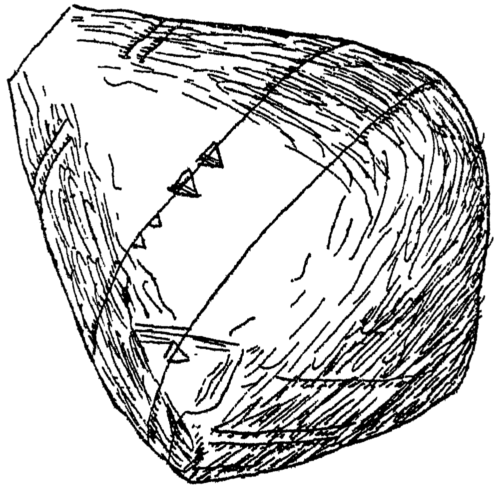

FIG. II.—Laminated Wesselton Diamond, enlarged.

Geometrically, the shorter diagonal of a rhomb of a dodecahedron coincides with an edge of the derived tetrahexahedron. The same rule is approximately true for such diamonds as are of good symmetry, and are not laminated; but when diamonds are laminated the rule is varied, in that the tetrahexahedron edge tends to slant away from its geometrical position into parallelism with the edges of the laminæ. This is, perhaps, the most important change made by the lamination on the aspect of a stone.

Fersmann and Goldschmidt have described ("Der Diamant," 1911) three laminated diamonds, all Brazilian, namely: Crystal No. 26, an irregular lump of a weak violet colour, showing lamination in three directions; Crystal 32, a brownish regular dodecahedron, whose surface is covered by a delicate network formed of innumerable twin lamellæ in four sets; and Crystal 33, a brown dodecahedron with coarse lamination. They argue that most diamonds may be presumed to be composed of such lamellæ, and that the lamination is brought into view by the process of solution. They seem further to hold that hemitropic twinning is the cause of the phenomenon. It is curious that their drawings of crystals 32 and 33 show the protruding edges of the lamellæ as running nearly parallel with the edges of the rhombs, a feature not actually possible in nature. Indeed, in this respect their version of the aspect of 33 differs absolutely from that of Rose and Sadebeck, made some 40 years earlier, and which they reproduce for comparison with their own.

Boutan also regards these laminated diamonds as macles by hemitrophy. He further regards Brewster's celebrated lens of diamond as having been cut from a multiple twin of this kind—a remote possibility, maybe, though not quite a probability, if only for the reason that a laminated stone is not likely to be transparent enough to serve as a good lens.

One reason against hemitrophy is that one sometimes comes across laminated stones which could just as well be called in the French way "macles by penetration," *i.e.*, tending to conform geometrically to the interpenetrating twins of the plus and minus tetrahedra; the lamination giving a terraced aspect to the blunt protruding pyramidal bosses very like the terraced diamonds from Jagersfontein in miniature. Another reason is that lamination is limited to four definite directions each of which is parallel to an octahedron face, so that in any laminated stone each multiple twin set intersects another at a constant angle; and this is the case even when the specimen is a macle. But macles when they intersect one another are not limited to definite directions at all; their seams crossing almost at random much as irregularly twinned simple crystals interpenetrate.

Lamination has an intimate correlation with colour. With very few exceptions, all laminated diamonds, no matter where they come from, are coloured—brown, mauve, green, or blue-white. Slight lamination may also be seen once in a way on poor cape-white diamonds, and on poor yellow ones. Reflexively, nearly every brown, and nearly every mauve, dodecahedral diamond, either macle or simple crystal, whether the tint be light or dark, is plainly laminated. (The featureless brown diamonds of resinous lustre from South-West Africa do not show lamination so often as brown diamonds from other sources. For that matter South-West African diamonds seldom show any surface detail at all to speak of, saving either an exceedingly high polish or a roughening due perhaps to wind erosion). So are most blue-whites when they are of a milky transparency or when their tint inclines to mauve. Lamination also occurs among the green diamonds from the Rand banket.

Hitherto I have only succeeded once in seeing signs of lamination in the interior of a diamond. This was in an ugly dark-brown brilliant in which the lamellæ were marked out in alternating lighter and darker brown streaks. A fair inference seems to be that a diamond going in general through stages of growth and quiescence may, during the latter, become covered with colouring matter which is enclosed in a later growth. The apparent uniform tint of the final whole stone will be largely a refraction effect (like the grey colour imparted to coated stones by indefinitely thin layers of tiny black spots), and is the happier as the laminæ are thinner. Thus the colouring matter is an overgrowth which establishes the lamination. There is no doubt that Heddle when he alleged the disseveration of "plate diamonds" ("Ency. Brit.," 9th Ed., Art. "Mineralogy"), was confounding the mythical bursting of smoky stones with the lamination of brown ones.

(*Addendum.*—While the above paper was going through the press I had the good fortune to see a most important specimen of diamond embedded in calcite, found by Mr. J. T. Vigne in the working over of some old Kimberley lumps. The diamond appears to be of about four carats, and the enclosing calcite perhaps five carats. The dia-

mond has evidently not been squeezed into the calcite, but has acted as a nucleus upon which the latter has crystallised. Mr. J. Stewart has, also, given me a portion of a beautiful shell of calcite taken from a Wesselton blue-ground diamond. The interior faces of this shell have acquired, from their intimate contact with the diamond, an almost perfect adamantine lustre).

## FURTHER STUDIES CONCERNING GALLIUM.

### ITS ELECTROLYTIC BEHAVIOUR, PURIFICATION, MELTING POINT, DENSITY, COEFFICIENT OF EXPANSION, COMPRESSIBILITY, SURFACE TENSION, AND LATENT HEAT OF FUSION.*

By THEODORE W RICHARDS and SYLVES ER BOYER.

### *I. Electrolytic Behaviour.*

INTRODUCTION.—The study of the electrolytic behaviour of gallium naturally had precedence in this investigation, because this behaviour had an important bearing on the preparation of the material needed for the rest of the work. The earlier experimenters upon gallium commonly used electrolysis rather as a means of precipitating the metal from purified salts than as a means of purification. In a recent paper, Dennis and Bridgman have pointed out the value of electrolysis for the latter purpose (Dennis and Bridgman, *Jour. Amer. Chem. Soc.*, 1918, xl., 1540; on p. 1537 references to earlier work are given). Independently, we also had simultaneously thus used electrolysis (Richards and Boyer, *ibid.*, 1919, xli., 133) Whereas the earlier experimenters commonly used alkaline solutions, Dennis and Bridgman, as well as ourselves, worked with more or less acid ones, free from alkali salts, thus eliminating the danger of contamination with alkali metals.

Although in the main the verdicts of the recent researches agree, several obscure points need elucidation before the matter is entirely consistent and comprehensible. The points especially to be investigated were the following: first, the single electrode potential of gallium, and secondly, the order of precipitation of indium, zinc, and gallium, with several different current densities from solutions of several different acidities.

*The Single Electrode Potential of Gallium.*—No adequate measurements of this potential appear in the literature, but the element is usually considered as coming between zinc (0·52) and aluminium (1·0), being nearer to that of zinc (see for example, Abeg's "Handbuch der anorg. Chem.," 1906, iii., [1], p. 367; *Compt. Rend.*, 1875, lxxxi., 493). This conclusion is based upon the earlier work of Lecoq and Boisbaudran.

For our measurements an accurate potentiometer, standardised by means of a Weston cell, was used. Cadmium and zinc were also measured against a calomel electrode in order to be certain that the apparatus was functioning properly. The single potential difference of cadmium in normal solution of its sulphate was found to be 0·176, and that of zinc in normal solution of its sulphate, 0·521. Hence the apparatus was adequate. Care was taken, in many of the trials, to have solutions of gallium sulphate neither basic nor with excess of acid, by converting weighed amounts of gallium (through the nitrate and weighed amounts of sulphuric acid) into sulphate. These precautions were, however, probably not necessary, because a small concentration of free acid does not usually much affect a single electrode potential. With amalgamated zinc, for example, 3 $N$ sulphuric acid was found by rough measurements to affect the potential by less than 0·05 volt. The potential of the decinormal electrode was assumed to be +0·56 volt. No allowance was made for the unknown solution-solution e. m. f.

In every case gallium showed at first a much smaller negative potential than the final value. With metal which had been exposed for a long time to the air the initial value was even positive (as much as 0·2 volt). In the course of two or three days the gallium potential gradually attained the maximum value —0·297 in 0·1 $N$ solutions; somewhat less (—0·25) in $N$ solutions, and even less when excess of sulphuric acid was present. 0·1 $N$ gallium alum as electrolyte gave about the same potential (—0·294 volt) as pure 0·1 $N$ gallium sulphate.

Adequate comparison of the effects of ion concentration, corresponding to the Nernst equation, can hardly be made, because the ion-concentration of gallium sulphate has never been determined. The substance is much hydrolysed, and probably hydrolysis diminishes the concentration of the gallium ion in dilute solution, making a colloidal hydroxide.

Liquid gallium *decreased* in potential with the time of immersion, to a lower value (—0·18) than the solid. Resolidification reversed this effect, but the gallium thus liquefied never assumed the value it would have had if its potential had been first determined as a crystalline solid. The decrease was hardly consistent enough to substantiate Rudorf's conclusions (Rudorf, Abegg's "Handbuch," *loc. cit.*, p. 366) concerning the free energy of the liquid based on Regnauld's measurements (J. Regnauld, *Compt. Rend.*, 1878, lxxxvi., 1457 (not Regnault, as Abegg gives the name).

Whichever final value is chosen from the abovementioned results, the single electrode potential of gallium thus measured stands between that of indium (—0·10) and that of zinc (—0·52). This was one reason for the statement to that effect in our earlier paper, because preliminary measurements of the electrode potential had been made before that paper was published. It will be seen, however, that this outcome gives an incomplete picture of the situation.

Another method of attacking qualitatively the problem of relative electrode-potential is by placing one metal in the solution of the salt of another, in order to determine if the second metal is precipitated at the expense of the first. De Boisbaudron's description of his result in this direction is not easily interpreted, but the simple experiment seemed worth repeating. Accordingly small amounts of fresh electrolytically precipitated zinc were placed in two portions of 5 cc. each of $N$ gallium-sulphate solution. After 15 hours, most of the gallium was precipitated in the form of a voluminous semigelatinous, white basic precipitate. In one case the slight metallic residue (after thorough washing, and the solution of

* From the *Journal of the American Chemical Society*, February, 1921

the zinc in very dilute acid), gave spectroscopic evidence of gallium—but the amount was only a very small fraction of the whole, and may have been due to inclusion. Evidently zinc does not precipitate metallic gallium in the definite fashion in which, for example, it precipitates cadmium.

The contrasting experiment of placing gallium in a nearly neutral zinc-sulphate solution was likewise made. After standing for 24 hours, the nugget of gallium showed no sign of a "tree," even in the microscope, and its surface appeared almost, if not quite, as bright as at first. Evidently gallium does not precipitate zinc.

When a solid alloy of gallium and zinc is treated with a little diluted sulphuric acid, both zinc and gallium are dissolved until the acid is exhausted, and no "tree" of either metal forms on the etched and pitted button.

These qualitative experiments leave one still largely at a loss with regard to the electrode potential of gallium. They seem to indicate that this quantity may be nearly the same as that of zinc.

A clue to the answer to the puzzle was afforded by the following experiments. Small fragments of the purest gallium, freshly cut, were placed in solutions of cadmium sulphate and of copper sulphate. Neither fragment showed more than a very slight tendency to precipitate these metals, each of which (especially copper), must have a lower solution tension than gallium. After six hours no evidence of precipitation at all was manifest, and even after several days, only a few minute spots of copper could be seen. (Afterward, following a suggestion by A. B. Lamb, copper chloride was tried. Here also the precipitation of copper was very slow in starting, but when once started it proceeded more rapidly with the chloride than with the sulphate). Clearly gallium, like its analogue aluminium (see for example v. Deventer and v. Lumnel, *Z. physik. Chem.*, 1909, lxix., 136), has a distinct tendency to become passive (or "ennobled"), which must vitiate all attempts to determine its true active electrode potential by the methods heretofore recounted. Accordingly, another line of attack was begun.

*The Electrolytic Precipitation of Gallium, Indium, and Zinc from Solutions of Varying Acidity and Concentration.*—The outcome of electrolytic precipitation depends, at least in part, of course, upon the electrode potentials of the substances concerned; but it depends also on at least three other conditions of electrolysis, namely, on the relative concentrations of the ions, on the current density at the cathode, and on "over-voltage" phenomena.

The effect of the concentration on the cation, as expressed by the Nernst equation, is well known. The solution tension of the solid metal is assumed to remain constant, but the effect of the opposing osmotic pressure of the cation increases with its logarithm; hence the single electrode potential decreases when the cation becomes more concentrated. For a trivalent ion such as indium or gallium, the theoretical increase in electromotive force is about 0·02 volt for each tenfold dilution at room temperatures. In order to change the electrode potential by as much as 0·1 volt, the solution must obviously be diluted to at least one hundred thousand times its original volume (or possess a concentration of 0·00001 of its original concentration). Hence this effect cannot play a very important rôle in causing two metals 0·2 or 0·3 volt apart in the electrochemical series to appear together.

As an example of the combined effect of changing current density and "over-voltage," the following fact may be cited. Zinc, although commonly possessing a far greater solution potential than hydrogen, can be precipitated in part from normal solution of the sulphate in the presence of $2N$ sulphuric acid by a current density of 0·4 amp./$cm^2$., whereas this precipitate will redissolve while the current is running if the current density is reduced to 0·2 amp./$cm^2$. In brief, there is a fairly definite relation between the current density, the concentration of the acid and the concentration of the metal which remains in solution after long-continued electrolysis. These considerations are of importance in interpreting the separation of metals electrolytically, especially if conclusions concerning relative electrode-potentials are sought.

The following experiments upon the electrolytic deposition of gallium, indium, and zinc, separately and together, were comprehensive, but will be summarised as briefly as possible. In all of these experiments sulphuric acid was present in definite, but not always identical, excess over the amount corresponding to the bases present. As the electrolysis proceeded, sodium hydroxide was added in amounts needed to neutralise the acid formed and keep the hydrogen-ion concentration about constant. The nature of the electrolytic precipitate was determined partly by its melting point, but usually by spectrum analysis. The three metals chiefly concerned (gallium, indium, and zinc) give clear spark- and arc- spectra, alone or together; our experience agrees with that of Dennis and Bridgman in showing that very small traces of each metal may be detected in the presence of the others. The characteristic lines, being in the blue and violet, are all easily photographed. Our comparisons were made almost entirely in this way with a good glass-prism spectrometer. The metals were volatilised by an arc spark obtained from a half kilowatt transformer from the 110 volt, 60 cycle, alternating current of the laboratory. The spark was intensified by a suitable condenser in parallel with the transformer, and the air lines were cut out by adequate inductance. Platinum points about 2 mm. in diameter were used as terminals of the spark gap, and the metals to be analysed were precipitated electrolytically directly upon the terminals, although these were not the electrodes of the fractional precipitation. Blank tests were frequent.

To recount first experiments upon the metals taken separately :—

Comparable results were obtained with platinum foil electrodes of 8 sq. cm. area and 0·3 ampere current (that is, an approximate current density of 0·04 amp. per sq. cm.). The volume of the solution in each case was about 100 cc. or less, and during the electrolysis each was continuously and thoroughly stirred by a mechanical stirrer. The amounts of indium, zinc, and gallium originally present were respectively about 0·4g., 0·2 g., and 0·1 g. The precipitated metal was completely transferred electrolytically from time to time to the spark gap terminals. With solutions of 0·2 $N$ acidity, about 0·6 mg. of indium remained per 100 cc. solution after 12 hours' electrolysis, four

times as much zinc and almost all the gallium present. Electrolysed in solutions of 0·1 $N$ acidity, all the indium was precipitated in 16 hours, about 1·2 mg. of zinc remained per 100 cc. solution after similar treatment, and distinctly more (90 mg. per 100 cc.) of the gallium. Zinc in a new trial was very nearly all precipitated in eight hours from a solution of 0·05 $N$ acidity, whereas 0·025 g. of gallium remained per 100 cc. of such solution after 13 hours. In a fourth trial after 17 hours even from a 0·04 $N$ acid solution, gallium was not fully precipitated, one mg. remaining per 100 cc. of electrolyte.

The results with more concentrated acid pointed in the same direction and need not be recounted in detail. No metal at all was precipitated by this low current density from a solution containing 0·4 g. per 100 cc. and 1·7 $N$ in sulphuric acid; very little indium, less zinc and no gallium from such a solution normal in sulphuric acid; and nearly all the indium, most of the zinc, and very little gallium even from a solution 0·5 $N$ in sulphuric acid.

These results are all consistent; they point indubitably to the following order of precipitation: indium, zinc, gallium, and indicate that, whatever the cause, gallium has a considerably higher deposition-potential than zinc in these acid solutions. But this result is inconsistent with the direct potential—measurements already recounted—for these placed gallium between indium and zinc.

Turning now to the electrolysis of mixtures, the following methods were used and results obtained.

The volume was in each case about 0·5 litre; the same current density as before (namely, 0·04 amperes per square cm.) was maintained; and the acidity was initially 0·15 $N$. When precipitation was almost finished, the acidity was reduced in order to recover all of the gallium. Six successive electrolyses of mixtures were conducted. In every case zinc was detected in the first precipitate (which was chiefly indium) and it was found at every stage of the electrolysis, successive portions of the precipitate being taken out and examined spectroscopically. Evidently indium and zinc are too near together to allow easy electrolytic separation, although theoretically their electromotive ranges should not seriously overlap; and the same is true of gallium and zinc. But in every case gallium began gradually to appear only after most of the indium had been precipitated. Hence these two metals are far enough apart to be easily separated.

Similar results were obtained with platinum points giving much greater current density, in strongly acid solutions. When a platinum point is used for deposition instead of a foil, the current density is so great that the ionised hydrogen in the immediate vicinity of the electrode is not enough to carry the current even when the solution is strongly acid. Hence other cations of greater solution potential may come down with the hydrogen. By preference, of course, those with smallest negative solution potential come out first. Thus, with a platinum point in 5$N$ sulphuric acid, we found that almost pure indium with melting point 155° came first out of a mixture of the three metals under consideration, if sufficient current density were used to precipitate anything besides hydrogen.

When only a small amount of zinc was present in the electrolysis conducted in this way, most of it appeared in the final deposit obtained after neutralising the free acid. This fact is in accord with the results obtained with zinc alone, in which it was shown that this metal cannot be precipitated completely by current density 0·04 from a solution 0·1 $N$ in acid.

Thus there is no real inconsistency between our results and those of Dennis and Bridgman. Different conditions produced different results. The amount of zinc in the specimen involved in our early trials was so small that little of it could be deposited by the current density and with the acidity then employed. Hence, most of the zinc remained in the electrolyte to the end and the order of deposition in this case was gallium, indium, zinc, as stated. The fact that most of the zinc was deposited in the early part of the electrolysis of Dennis and Bridgman is easily explained if their solution (as is probable from their description) was decidedly less strongly acid than ours.

The explanation of the apparent inconsistency between the relative magnitude of the electrode-potentials and the order of actual deposition seems to indicate that gallium possesses a larger negative electrode-potential in the act of depositing from a solution than it possesses when actually deposited. In other words, it probably possesses some degree of "passivity" when in a metallic state, as already indicated by other tests. This conclusion is supported by the fact that gallium is markedly passive toward dilute nitric acid, although it dissolves in concentrated nitric acid It seems to occupy a place, in this respect, between indium, which dissolves easily in nitric acid of any concentration, on the one hand, and aluminium, which is passive towards dilute sulphuric and concentrated nitric acid, on the other hand. Our experiments on electrode-potential indicated that liquid gallium is even more passive than the solid. This agrees with the fact that liquid gallium is less easily attacked by acids than solid gallium, although this fact may be due, as Rudorf has pointed out (Rudorf, Abegg's "Handbuch," *loc. cit.*), merely to the possession of more points of attack in the solid. All these questions will receive more detailed examination here in the near future. An answer to the vexed question as to the cause of passivity in general, or of this case in particular, is left in abeyance for the present.

### *II. Purification of Gallium.*

The foregoing statements make clear the advantage of electrolysis as a first step in purification. The elimination of indium and all metals of lower solution tension is easy by this means. Accordingly this method was used as an initial step in the purification of the large quantity of gallium needed later for determining the properties of this substance.

The choice of electrodes for electrolysis was made with care. The liquid metal alloys with silver, making it brittle; and the deposited gallium contains dissolved silver. Hence this metal is entirely unsuitable. Iron seems to show in less degree a similar effect, except that the solid alloy is soft instead of being brittle. Gallium alloys slightly even with platinum foil, which is blackened afterwards by acid. Moreover, the

liquid gallium removed from this platinum foil may contain traces of platinum.

A point of wire is evidently safer than a large piece of foil, since the action of one metal upon the other can take place only on the surfaces where they adjoin. Thus gallium from an iron point was found to contain no appreciable iron. That from a platinum point is even safer, since platinum is attacked less than iron is. Finally, in preparing our purest material we used as the electrode a gallium cathode contained in a cup and making contact beneath its surface with a platinum point of minimum dimensions.

During the electrolysis of a solution of the raw material (a crude gallium indium alloy) the hydrogen evolved was found to give a mirror in the Berzelius-Marsh apparatus. Part of this sublimate was shown to be arsenic, and germanium was indicated by the line 4033, although the two more prominent lines, 4227 and 4180, were often absent. A line very close to 4058 was likewise found. This was most probably due to lead, although this metal does not ordinarily form a volatile compound with hydrogen on electrolysis. It is true that Panett and Fürth (Panett and Fürth, *Ber.*, 1919, lii., 2020) state that they have found such a compound (the particulars to be given later) but we have not been able to reproduce it. Whether the apparent presence of lead and also trace of zinc in the Marsh-Berzelius mirror were due merely to the spattering (which, however, had been carefully guarded against) or to traces of volatile compounds we do not pretend to decide. That arsenic was present there could be no doubt. The spectrum was compared with the spectrum of pure arsenic in a Plücker tube at 220° to 230°, taking the helpful precautions of Herpertz (Herpertz, *Dissertation*, Bonn, 1906). The suitable vacuum was obtained by a Langmuir pump.

Incidentally, mention may be made of a black precipitate consisting chiefly of gallium, and of a spongy aggregation which appears at the cathode under some conditions, the latter especially when the solution is almost neutral. It was easy to prove that both consisted of metallic gallium mixed with a trace of basic salt and bubbles of hydrogen which prevent its complete coherence.

Gallium deposited from the solution of the crude liquid alloy, when most of the indium had been separated electrolytically, contained considerable zinc. This could be, in part, eliminated by fractional electrolysis, but the process is slow, as may be inferred from the foregoing account.

Two methods were therefore employed which were found to be effectual in removing the last trace of this metal, namely, ignition at a red heat in a vacuum (when zinc distils by virtue of its lower boiling point) and fractional crystallisation of the gallium with centrifugal draining (when all heteromorphous materials remain in the liquid).

The purification by heating in vacuum is most conveniently carried out by placing the electrolytic metal in a silica boat enclosed in a silica tube, and heating for several hours in a good vacuum until the boat-load remains almost constant in weight. Complete constancy is not attained, since gallium itself is slightly volatile at 800°. The sublimate was shown by suitable qualitative tests to consist chiefly of zinc. The residue from this treatment must still have contained a trace of some unknown impurity since its melting point was still not quite constant.

Fractional crystallisation of the metal was the method used to complete the purification. Liquid gallium, supercooled to a temperature slightly below its true freezing point, was inoculated with a trace of the solid phase, introduced on a platinum point Crystals of gallium 4 to 6 mm. in length were allowed to form slowly. Consisting of the purer gallium, these crystals were removed, but upon their surface they carried some of the less pure liquid. This was removed by means of a hand centrifuge, the inner vessel of which consisted essentially of a test-tube with a much constricted place near the bottom. The crystals of gallium rested upon the constriction, and the liquid was driven by centrifugal force through the narrow opening, while the test-tube, resting upon a pad of cotton wool in a hollow wooden cylinder attached to a stout leather strap, was whirled in a two-metre circle. Before the slightly warm glass vessel was placed in the wooden receptacle, the latter had been warmed to 32° in order to prevent solidification of the adhering liquid before the centrifuging was complete. Two or three successive recrystallisations were enough to bring the purest fraction to a constant melting point, but in order to economise the small amount of fairly pure electrolytic material at our disposal as much as possible, many systematic recrystallisations from the mother liquors were conducted, thus purifying more of the gallium.

In all 10·4 g. of pure gallium of constant melting point (that is, showing no change in melting point from the beginning to the end of liquefaction) was separated from about 15g. of the less pure electrolytic metal. This specimen was called Sample E.

### *III. The Melting Point of Gallium.*

De Boisbaudran, in successive trials, at first found the melting point of gallium to be 29·5°, and later 30·15°, with very small amounts of material (*Compt. Rend.*, 1876, lxxxii., 1036; 1876, lxxxiii., 611). More recently, Browning and Uhler found the value 29·7° by reading the temperature at which globules of solid gallium fell through a slightly smaller platinum ring (*Am. J. Sci.*, 1916, [4] xlii., 389). Neither experimenter mentions the precautions taken with regard to standardising the thermometers; and judging from our experience, probably neither had perfectly pure gallium.

Our own preliminary experiments, made by watching a crystal of the metal (either at the bottom of a small test-tube or suspended in a ring immersed beneath a slowly changing bath) usually gave too high results because of convection currents, and the lag in temperature of the metal. Methods of this sort led to the value 30·8° (which we found subsequently to be about a degree too high) for the melting point of our best gallium. An accurate determination of a melting point can hardly be made unless enough of the substance is at hand wholly to surround the registering instrument with a mixture of the two phases whose equilibrium is concerned. Therefore we did not succeed in obtaining satisfactory values until we used a much larger quantity of the metal.

Two methods were finally employed. First, the gallium was melted in a small air-jacketed test-tube in an easily adjustable thermostat, after the fashion of the Beckmann freezing-point apparatus, or that so often used by one of us for taking transition temperatures (see for example, Richards and Wells, *Proc. Am. Acad.*, 1902, xxxviii., 431; *Z. physik. Chem.*, 1903, xliii., 465). In this apparatus about 10 g. of the best gallium was used. Its melting point remained constant until only a very few crystals remained

Another method which gave precisely the same result consisted in determining the temperature at which a glass-stoppered dilatometer, filled with a mixture of crystallised and liquid gallium under water, showed neither decrease nor increase in the volume of its contents with time. About 8·5 g. of crystallised gallium was used. The water was pure and was freshly boiled and quickly cooled; so prepared it does not oxidise gallium seriously in a few hours. The scale on the capillary of the dilatometer showed change of about 0·4 mm. during the melting of 0·01 g. of gallium. The dilatometer was immersed to the beginning of the index tube in a thermostat at 29°, and the temperature was slowly raised until melting was indicated by the sinking of the water level in the capillary. After perhaps a quarter of the metal had melted, the temperature was slowly lowered until the column remained stationary.

The small thermometer used with each method was very carefully standardised with reference to the Parisian hydrogen scale through one of the Harvard Baudin thermometers, both being read with a cathetometer to within 0·002°.

The direct determination of the melting-point in the small Beckmann apparatus gave the value 29·752° for the melting point. With the dilatometer method, at 29·755°, the column slowly descended, whereas at 29·745 it slowly rose, indicating the value 29·75° as the true melting point. Since the two methods agreed, this value (29·75°) may be taken as correct for the purest gallium which we have thus far prepared.

*IV. Density of Solid and Liquid Gallium.*

The striking expansion of gallium upon solidifying is of peculiar interest, since this property is possessed by so few substances. Some previous investigators have ascribed it to the presence of impurities (Rudorf, Abegg's "Handbuch," *loc. cit.*). The work which follows shows, however, that undoubtedly the purest gallium behaves in the same way as the somewhat impure metal first studied.

The form of pycnometer employed was that used recently in the determination of the density of lead isotopes (Richards and Wadsworth, *Journ. Am. Chem. Soc.*, 1916, xxxviii., 222). All the usual precautions were taken to ensure constancy and definiteness of temperature, absence of air bubbles (the pycnometer was filled in a vacuum) and protection from evaporation. Both the solid and liquid gallium were weighed under freshly boiled and quickly cooled pure water. Without precautions, gallium, on solidifying in a pycnometer invariably breaks it by the expansion which then occurs; but if the pycnometer is constantly agitated during slow cooling the crystalline mass does not attach itself to the vessel, nor subject the walls to outward pressure. If solidification against the walls begins to take place, it is easily overcome by partial melting and resolidification. When the density of the liquid was determined after that of the solid, the pycnometer was placed in an evacuated vessel in order to remove any trace of hydrogen which might have been formed by the long standing under water. Promptness is advisable since even with the purest water a slight action takes place after a number of hours, and, of course, both bubbles of gas and the film of oxide cause a decrease in the observed density of the metal.

The densities of a number of samples were determined The first sample, A, contained several per cent of indium and a trace of zinc. It was obtained from the hydroxide dissolved in sodium hydroxide, which carries with it indium hydroxide. From Sample B most of the indium had been removed by fractional electrolysis. Sample C had been refractionated electrolytically from a solution 2 $N$ in free sulphuric acid and the metal had been heated in a vacuum for three hours to expel zinc. Sample $C_2$ was another preparation of the same kind. Neither was entirely free from impurities. Therefore Sample D was prepared with much greater care by fractional electrolysis, but it began to melt on the surface 0·2° below the true melting point of gallium. Sample E, the purest, has already been described above.

(To be continued.)

## THE CHEMICAL INDUSTRY IN THE ARGENTINE REPUBLIC.

THREE Argentine companies manufacture sulphuric acid (53°-56° Baumé) by the chamber process with imported sulphur from Italy, Chile, and the United States. There is a great demand for Sicilian sulphur, since, being of greater purity, and burning without ash. Transport of sulphuric acid by sea is very difficult, owing to long voyages in the tropics, the home industry being thus favoured. Nevertheless, local works find it difficult to compete with imports.

Nitric and hydrochloric acids, the first in commercial degrees (38° and 42°), are manufactured from Chile saltpetre and native salt. Chemically pure sulphuric and hydrochloric acids are, however, manufactured. The main part of the acetic acid imported is glacial, at 99°. Two works near Cordoba produce pyroligneous products by dry distillation of algarrobo wood, chiefly acetates of lead and lime acetone, acetic acid, which are more expensive than imports. However, the demand exceeds the supply. Local production of tartaric acid is limited to one or two vineyards, wine lees being obtained in large quantity at Mendoza. In 1916 the United States began to export this acid to the Argentine. During the last eight years, imports of citric acid from France, England, Germany, and Italy, represented an average of 132 metric tons per year. The United States commenced exports in 1914. The acids sell better in crystals than powder. Imports of phenic acid are very irregular; England is the chief manufacturer. Tar oil acids are preferred to wash cattle.

The oils should contain at least 10 per cent phenol, and some manufacturers say 25 per cent. Boric, carbonic, hydrofluoric, and tannic acids are also imported from Germany, France, England, and, since 1916, the United States has supplied a certain amount of carbonic acid. Gaseous carbonic acid is manufactured locally in breweries. Imports of alum, which were more than 6300 metric tons from 1913 to 1916, fell to 490 tons during the last two years. The United States imports now represent 50 per cent. Hydrated alumina is employed to a limited degree for lakes and colours, textiles and glass. Large quantities of home-made sulphate of aluminium are employed to purify drinking water in Buenos Ayres, &c. Local manufacture is only one-quarter of the imports. Ammonia is chiefly imported. The average imports during the last seven years were 540 metric tons per year, 90 per cent being from America. Liquid ammonia is chiefly English. Arsenic and arsenical compounds are employed for glass, insecticides, and colours. The demand is for white, yellow, and red arsenic (99 per cent), in barrels of 200 kilogrms., and arseniates of lead and soda in boxes of 5 kilogrms. The United States now heads the list of imports.—*Chimie et Industrie*, February, 1921.

## PROCEEDINGS OF SOCIETIES.

### MINERALOGICAL SOCIETY.

*March* 22, 1921.

DR. A. E. H. TUTTON, F.R.S., in the Chair.

THE following papers were read:—

"*The Vibrations of a Crystalline Medium.*" By Prof. H. HILTON.

The paper attempts to give an indication of the kind of vibrations which the molecules of a crystal may be expected to make about their positions of equilibrium. The case of an orthorhombic crystal in the form of a rectangular parallelepiped is considered in detail, and the normal modes of the molecular motion completely determined.

"*Augite from Nishigatake, Japan.*" By Prof. R. OHASHI.

The crystals have been detached from basalt by natural weathering. Specific gravity is 3·338 at 4° C. The prism angle agrees with that of diopside, but that of the pyramid does not. Etched figures show that the crystal belongs to the holosymmetric class $\alpha=1{\cdot}6859$, $\beta=1{\cdot}6917$, $\gamma=1{\cdot}7105$, $2v=58°\ 25'$. Extinction angle on (010)=41·6°. The chemical composition is $SiO_2$ 51·37, $Al_2O_3$ 5·24, $Fe_2O_3$ 2·02, FeO 2·96, CaO 21·58, MgO 16·94, $TiO_2$ 0·58. Both the optical properties and chemical composition show that in this augite the diopside molecule predominates.

"*The Chemical Composition of the Adare and Ensisheim Meteorites.*" By Dr. G. T. PRIOR.

Determination of the amount and composition of the nickeliferous iron in these meteorites had shown that Adare contained 18 per cent, in which Fe : Ni=11, and Ensisheim 3 in which Fe : Ni=3½. Analyses were made of the unattracted material in order to determine how far they supported the idea that in meteoric stones the ratio of MgO to FeO in the magnesium silicates varied directly with the ratio of Fe to Ni in the nickel-iron. The results showed that the ratios of MgO to FeO in the olivine and pyroxene respectively were about 4 or 5 for Adare, and 2½ and 3 for Ensisheim.

Mr. W. BARLOW exhibited models to represent the atomic structure of calcite and arragonite.

## NOTES.

ROYAL SOCIETY.—At the Meeting of June 2, the Bakerian Lecture will be delivered by Dr. T. M. Lowry, F.R.S., and Dr. P. C. Austin, on "Optical Rotatory Dispersion."

ROYAL INSTITUTION.—A General Meeting of the Members was held on April 4, Sir James Reid, Bart., Vice-President, in the Chair. Mr. S. D. Bles, Mr. S. T. Covington, Mrs. L. W. Dent, Mr. B. G. Donne, Prof. Godfrey, Com. A. C. Goolden, Mr. A. Mallalieu, Mr. W. Marshall, Mr. E. W. T. L. Brewer Williams, and Sir John Wormald were elected Members. The Chairman reported the death of Lord Moulton, a Member of the Institution, and a resolution of condolence with the relatives was passed.

ROYAL INSTITUTION.—On Tuesday next, April 19, at 3 o'clock, Prof. Arthur Keith resumes his Lectures at the Royal Institution on "Darwin's Theory of Man's Origin (In the Light of Present-Day Evidence)"; on Thursday, April 21, Mr. H. S. Foxwell begins a course of two lectures on "Nationalisation and Bureaucracy"; and on April 23, Mr. H. Y. Oldham delivers the first of two lectures on the "Great Epoch of Exploration: (1) Portugal; (2) Spain." The Friday evening Discourse on April 22 will be delivered by Sir James Walker on "Electro-Synthesis in Organic Chemistry," and on April 29 by Sir Frank Dyson on "Advances in Astronomy."

MARKET FOR ANT EXTERMINATORS IN COLOMBIA. —The Commercial Secretary to H.M. Legation at Bogota (Lt.-Col. G. W. Rhys Jenkins) reports that there is an urgent demand in the Santa Marta district for a good ant exterminator for use on the local coffee plantations. It appears that practically all the estates are infested with quantities of large brown ants, which devour everything in sight, including the young coffee shrubs. The Commercial Secretary has received an enquiry as to United Kingdom sources of supply of a suitable exterminator, and particulars will be furnished to any United Kingdom firms interested, on application to the Department of Overseas Trade (Development and Intelligence), 35, Old Queen Street, London, S.W.1.

THE AUTOMATIC FURNACES, LTD., have issued a small pamphlet presenting some carefully arranged data on the effects of overheating high carbon steel. The Company have for years specialised in precision heat treatment of steel, and now are undertaking to harden samples of manufacturers' own tools for a comparative test against similar articles hardened by the maker. The pamphlet in question and full information can be obtained at the Company's offices, 281-283, Grays Inn Road, W.C.1.

At the recent Guthrie Lecture at the Physical Society, Prof. A. A. Michelson, of the University of Chicago, took as his subject "Some Recent Applications of Interference Methods," and gave details of his recent work on the Measurement of Earth Tides, A Redetermination of the Velocity of Light, and the Measurement of the Diameters of Fixed Stars.

Iron and Steel Institute.—The Annual Meeting of the Institute will be held, by kind permission, at the Institution of Civil Engineers, Great George Street, Westminster, on Thursday and Friday, May 5 and 6, 1921, commencing each day at 10 a.m. Thursday, May 5—General Meeting of Members; a selection of Papers will be read and discussed. Friday, May 6—Annual General Meeting. The following is a list of the Papers which it is expected will be submitted :—

"The Prevention of Hardening Cracks, and the Effect of Controlling the Recalescence of a Tungsten Tool Steel." By S. N. Brayshaw.
"The Welding of Steel in Relation to the Occurrence of Pipe Blow Holes and Segregates in Ingots." By H. Brearley.
"Open-hearth and other Slags—their Composition and Graphic Methods for Determining their Constitution." By J. E. Fletcher.
"Notes on the Cleaning of Blast-Furnace Gas." By S. H. Fowles.
"The Protection of Iron with Paint against Atmospheric Corrosion." By J. Newton Friend.
"On the Cause of Quenching Cracks." By K. Honda, T. Matsushita, and S. Idei.
"Slip-Lines and Twinning in Electro-Deposited Iron." By W. E. Hughes.
"Scientific Control of Combustion." By H. T. Ringrose.
"Comparison of Different Methods of Estimating Sulphur in Steel." By T. E. Rooney.
"Solid Solution of Oxygen in Iron." By J. E. Stead, F.R.S.
"Roentgen Spectographic Investigations of Iron and Steel." By A. Westgren.
"Cupric Etching Effects Produced by Phosphorus and Oxygen in Iron." By J. H. Whiteley.

## New Patents.

This List is specially compiled for the *Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, W.C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

9203—Benko, R.—Manufacture of iodine, etc., compounds. March 26th.
8988—Chemische Fabrik Weissentien Gess.—Process for distilling sulphuric acid. March 23.
8858—Craig, E. N.—Reduction of oxides of tungsten and molybdenum. March 22.

*Specifications published this Week.*

160185—Marks, E. C. R.—Process for production of reactive acid liquor alcohols, esters, and the like from olefine hydrocarbons.
160258—Vickers, Ltd.—Toco Rubber and Waterproofing Co., Ltd. and Nuttall, W. H. Condensation of phenolic bodies with aldehydic compounds.
139803—Chemical Construction Co.—Apparatus for the manufacture of superphosphate of lime and similar compounds.

*Abstract Published this Week.*

Messrs. Boake Roberts & Co. of Stratford, London, have been granted a patent No 157578, for a process of obtaining Diethy-sulphate. It is prepared by passing ethylene in great excess into sulphuric acid, containing 81-100 per cent $H_2SO_4$, or into oleum containing up to 90 50, at a temperature of 120° C. Ethyl hydrogen sulphate is first formed and this is converted into diethyl sulphate by continuing the introduction of ethylene until the weight of the reaction has increased by at least 20 per cent of the weight of sulphuric acid present.

Ethyl hydrogen sulphate in any known manner may be used in the first instance as the absorbent for the ethylene.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

## MEETINGS FOR THE WEEK

*Monday, April 18.*

Royal Society of Arts, 8. "Recent Applications of the Spectroscope and the Spectrophotometer to Science and Industry" by Dr. Samuel Judd Lewis.

*Tuesday, April 19.*

Royal Institution, 3. "Darwin's Theory of Man's Origin" by Prof. A. Keith.

Institution of Petroleum Technologists, 5.30.

*Wednesday, April 20.*

Royal Society of Arts, 4.30. "Thomson's Apparatus for Armless Men" by Sir James Cantlie.

Royal Microscopical Society, 8.

*Thursday, April 21.*

Royal Institution, 3. "Nationalisation and Bureaucracy" by Prof. H. S. Foxwell.

Institution of Mining and Metallurgy, 5.30.

Chemical Society, 8.

*Friday, April 22.*

Royal Institution, 9. "Electro-Synthesis in Organic Chemistry" by Sir James Walker.

Royal Society of Arts, 4.30. "The Common Service of the British and Indian Peoples to the World" by Col. Sir Edward W. H. Gregg.

Technical Inspection Association, 7.30. "Physical Properties of Clay" by Alfred S. E. Ackermann.

Physical Society, 5.

*Saturday, April 23.*

Royal Institution, 3. "The Great Epoch of Exploration—Portugal" by Dr. H. Y. Oldham.

## NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemical Apparatus, &c., for review or notice to be addressed to the EDITOR.

**SUBSCRIPTIONS**, £1 12s. per annum, payable in advance, should be addressed to the MANAGER.

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# THE CHEMICAL NEWS.

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## FURTHER STUDIES CONCERNING GALLIUM.

### ITS ELECTROLYTIC BEHAVIOUR, PURIFICATION, MELTING POINT, DENSITY, COEFFICIENT OF EXPANSION, COMPRESSIBILITY, SURFACE TENSION, AND LATENT HEAT OF FUSION.*

By THEODORE W. RICHARDS and SYLVESTER BOYER.

(Continued from p. 177.)

THE results for the density of the less pure material need not be given in full, but will be summarised.

Sample A (containing indium) was found, as an average of a number of determinations, to have the density of 6·162 as liquid at 29° and 5·975 as solid at 20°. No great difference was observed between the metal thus solidified in the pycnometer or solidified in air a little below the melting point on a block of paraffin. On the other hand, this impure gallium when solidified by dropping into cold water from a pipet, was found to give a lower result, about 5·90, probably due to included water, but possibly to be referred to the sudden solidification of a more bulky unstable alloy, which may not appear when the cooling is slow. Correcting the values for the solid to 29° by means of the coefficient of expansion, mentioned later, the value at 29° is found to be 5·974. The change in specific gravity of this impure sample on melting is therefore found to be 0·188; of Sample B, considerably purer, the change at 29°, corrected in the same fashion, was from 5·893 to 6·084, or 0·191; for sample C (several preparations) the average for four determinations of the solid was found to be 5·889, whereas four determinations of the liquid gave the value 6·079, a difference of 0·190.

Sample D, which was very nearly, but not perfectly, pure, gave, with three different preparations, the following values (two apiece) for the liquid at 29·8°, 6·090, 6·094, 6·093, 6·097, 6·098, 6·099; an average of 6·095, whereas for the solid at 29·6°, the following five values were found: 5·907, 5·908, 5·907, 5·905, 5·903, an average of 5·906, and a difference of 0·189.

The last and purest sample, E, gave essentially identical results, which are given in full in Table I. In these cases, the gallium was introduced into the pycnometer in the liquid state and solidified there under pure boiled water. The density of the solid was determined at 29·65°, and that of the liquid at 29·8° on the hydrogen scale.

The respective densities of pure liquid and solid at the melting point are, therefore, 6·0947 and 5·9037, the difference being 0·191; and the respective specific volumes of the two states of the metal are 0·16408 and 0·16939 cc., the difference being 0·00531 cc. Allowing for its coefficient of expansion, the density of the solid at 20° may be taken as 5·907 and its atomic volume as 11·85, if the atomic weight is 70·1.

Evidently, since the further purification between D and E produced no essential change in the density of either solid or liquid, and since the substance last measured had been heated for a long time in vacuum and purified by crystallisation, the densities recorded above for the gallium in the two states cannot be far from the truth. Table II., reiterating the change of density on crystallisation in the several specimens of increasing purity, shows conclusively that the impurities have nothing to do with the change of volume, since the variations are not greater than the possible variation due to experimental error.

TABLE II.

| Sample | Average density. Solid. | Average density. Liquid. | | Difference between density of solid and liquid. |
|---|---|---|---|---|
| A ... ... | 5·974 | 6·162 | More or less impure | 0·188 |
| B ... ... | 5·893 | 6·084 | | 0·191 |
| C .. .. | 5·889 | 6·079 | | 0·190 |
| D ... ... | 5·906 | 6·095 | Fairly pure | 0·189 |
| E ... ... | 5·904 | 6·095 | Very pure | 0·191 |

Supposing that no great contraction or expansion takes place when indium is dissolved in gallium (which seems reasonable because of the similarity of the two metals), the percentage of indium in Sample A (its specific gravity being 7·31), is easily calculated approximately from the liquid to be 5·6 per cent, and from the solid to be 4·8 per cent. Evidently, Sample A must have contained about 5 per cent of indium. If contraction occurred on the solution of one metal in the other, the percentage thus calculated would be higher than the true value, and *vice versa*.

* From the *Journal of the American Chemical Society*, February, 1921

TABLE I.—*Density of Gallium.*

| No. | Obs wt. Ga. | Wt. in vac. | Wt. $H_2O$ in vac. not displ. | Corrected vol. $H_2O$. | Vol. pyc. | Vol. $H_2O$ displ. | Dens W/V. |
|---|---|---|---|---|---|---|---|
| | | | (Liquid.) | | | | |
| 1 ... ... ... ... ... ... | 9·0447 | 9·0452 | 5·8956 | 5·9209 | 7·4056 | 1·4847 | 6·092 |
| 2 .. ... ... ... ... ... | 9·0447 | 9·0452 | 5·8959 | 5·9211 | 7·4056 | 1·4845 | 6·093 |
| 3 ... ... ... ... ... ... | 10·1864 | 10·1870 | 5·7104 | 5·7348 | 7·4056 | 1·6708 | 6·097 |
| 4 ... ... ... ... ... ... | 10·1864 | 10·1870 | 5·7103 | 5·7347 | 7·4056 | 1·6709 | 6·097 |
| | | | | | | Av. | 6·0947 |
| | | | (Solid.) | | | | |
| 1 ... ... ... ... ... | 9·0447 | 9·0452 | 5·8943 | 5·8740 | 7·4056 | 1·5316 | 5·905 |
| 2 ... ... ... ... ... | 9·0447 | 9·0452 | 5·8487 | 5·8734 | 7·4056 | 1·5322 | 5·903 |
| 3 ... ... ... ... ... | 10·1864 | 10·1870 | 5·6563 | 5·6802 | 7·4056 | 1·7254 | 5·904 |
| 4 ... ... ... ... ... | 10·1864 | 10·1870 | 5·6558 | 5·6797 | 7·4056 | 1·7259 | 5·903 |
| | | | | | | Av. | [illegible] |

### V. *The Cubical Coefficient of Expansion of Gallium.*

The direct measurement of the linear expansion of solid gallium was not easily made with the small amount of metal at hand, and, therefore, the cubical coefficient of expansion was found by determining the density of solid gallium at 0·1° and 29·65°. The volume of the pycnometer also was determined at 0·1° in order that any errors due to manipulation, to possible condensation of moisture on, or evaporation from, the pycnometer, &c., should be equalised. In this way in five experiments (from which the danger of condensation was excluded by warming the pycnometer before drying and weighing) the density varied between the extremes, 5·912 and 5·915, in average 5·9134 at 0·10 C., whereas the density at 29·65° had been found to be 5·9037. The increase in density is thus 0·0097, which corresponds to a cubical coefficient of expansion of 0·000055 or a linear coefficient of expansion of 0·000018.

Of course, any value obtained in this way has a large probable error, but it is better than nothing. This value is about one-third that for sodium, somewhat less than that for magnesium, aluminium, cadmium, thallium, or zinc, but not far from that for copper and silver. It is about midway between the values for zinc and arsenic, as would be expected from the fact that the atomic volume of gallium is also approximately midway between those of these two metals, near it on opposite sides in the periodic table (Richards, "Concerning the Compressibilities of the Elements, and Their Relations to Other Properties," *Journ. Amer. Chem. Soc.*, 1915, xxxvii., 1643; correction, 1915, xxxvii., 2696).

### VI. *The Compressibility of Gallium.*

The method and apparatus have already been described in detail (for example, Richards and Jones, *ibid.*, 1909, xxxi., 161). The form of piezometer first used for the liquid was essentially like that employed for determining the compressibility of the rubidium-potassium alloy (Richards and Stull, *Carnegie Inst. Pub.*, 1907, lxxvi., 19). If solidified in this apparatus the gallium, of course, would have burst the containing tube. For this reason gallium was cast in a separate small glass tube, producing a cylinder of the metal from which the broken fragments of glass were wholly removed. This cylinder was placed in a slightly larger test-tube, and this latter tube was capped with a long glass cap. The whole was then placed in a still larger test-tube that came almost to the top of the cap, and a platinum wire held the combination together. In this way, solid gallium could be compressed under mercury, but protected from this liquid by the toluene underneath the cap. The contrivance was less simple than that used later for determining the compressibility of indium (Richards and Sameshina, *Journ. Amer. Chem. Soc.*, 1920, xlii., 49), but was adopted in this case for fear of melting the gallium accidentally, when it would have immediately amalgamated with the mercury.

The weighing of the toluene and mercury (which had been purified by usual methods) was effected as follows. The cylinder of the solid metal was placed in the inner test-tube and this tube was next filled with toluene in a vacuum. The cap (filled with toluene) was then placed over the test-tube while immersed in a larger vessel containing toluene, and the capped tube was placed in the larger test-tube while still under the liquid. After wiring the tubes together, a weighed quantity of mercury was finally added to the outer tube, replacing the toluene, and also holding the toluene beneath the cap. Enough toluene was displaced so as to make sure that no more would be liberated from the cap accidentally, and all toluene was removed from the surface. Since the weights of the glass, gallium, and mercury were known, that of the toluene was found very simply by the difference. It is necessary in such a case to know the weight of the toluene with great accuracy, since its compressibility is 30 times as great as that of gallium.

The assembled apparatus was suspended in a piezometer, essentially like that used in earlier researches (Richards and Stull, *Carnegie Inst. Pub.*, lxxvi., p. 11, pattern V., Fig. 2). The samples of gallium of which the compressibility was determined have already been described as Sample C. The purest sample, E, could not be used for this work, since there was not enough of it; but the amount of impurities could not have been enough in Sample C to exceed the probable error of measurement in its effect.

Following are complete data of two determinations of gallium, together with the measurements made with the piezometer alone. The figures in the last column, for the range 100 to 400 megabars (the megabar is the "absolute atmosphere," or 0·983 of the ordinary "atmosphere"), were taken from curves carefully drawn through the points defined by the proceeding data.

In order to apply the large correction due to the presence of the toluene, 26·538, 25·719, and 25·939 g. of this hydrocarbon were compressed separately in Piezometer II. and found to need mercury additions of 11·105, 10·578, and 10·820 g. respectively, between 100 and 500 megabars. Subtracting from each the value which was obtained in this piezometer with mercury alone (0·249 g.) and dividing by the weight of toluene in each case, values for the difference in added mercury over this pressure range produced by one g. of toluene, 0·409, 0·402, and 0·408 are obtained, in mean 0·406. The presence of the additional glass had an effect (in the contrary direction) of 0·0032 per g. These values were substituted in the equations already given (the most convenient for this purpose have the form given in the *Journ. Am. Chem. Soc.*, 1915, xxxvii., 471, with the addition of another term, $0{\cdot}0032 \times 5{\cdot}86$ in the parenthesis in the numerator to account for the glass container within the piezometer).

TABLE III.—*Data for Compressibility of Solid Gallium* (*at* 20°).

I.—Piezometer with 429·2 g mercury alone.

| Press. range. | Wt. Hg. | Press. range. | Wt. Hg. | Wt. Hg for 400 megabars |
|---|---|---|---|---|
| 99·0-283·7 | (0·1256) | 283·7-478·7 | (0·1263) | 0·264 |
| 99·7-299·9 | (0·1334) | 299·9-495·9 | (0·1245) | 0·261 |
| 90·6-305·6 | (0·1412) | 305·6-499·0 | (0·1236) | 0·259 |
| | | | Av., | 0·261 |

II.—Piezometer I with 23·42 g. solid gallium, 0·871 g. toluene, and 5·86 g. glass test-tube con-

tainer (one of these trials was rejected as obviously in error, probably from a mistake in weighing).

| | | | | |
|---|---|---|---|---|
| 88·0-359·3 | (0·2397) | 357·3-496·3 | (0·5428) | 0·560 |
| 115·0-275·0 | (0·2397) | 275·0-505·3 | (0·5428) | 0·561 |
| 130·6-302·8 | (0·2505) | 302·8-513·5 | (0·5299) | 0·564 |
| | | | | Av., 0·562 |

III.—Piezometer I. with 19·47 g. solid gallium, 0·858 g. toluene, and 5·86 g. glass.

| | | | | |
|---|---|---|---|---|
| 115·9-298·0 | (0·2638) | 298·0-510·1 | (0·2716) | 0·548 |
| 107·1-303·9 | (0·2829) | 303·9-494·1 | (0·2472) | 0·549 |
| | | | | Av., 0·548 |

Thus two values for the compressibility of solid gallium are obtained: 0·0000024 and 0·0000016—in the mean 0·0000020. The comparatively poor agreement of the results is to be regretted; it is probably to be ascribed to the complication and consequent size of apparatus, adopted because of the low melting point of gallium. Although only preliminary, these results are, nevertheless, worth recording, since they are the only results for this constant which have been obtained.

Determinations of the compressibility of *liquid* gallium were less satisfactory and need not be recounted in detail; but they showed indubitably that liquid gallium is far more compressible than the solid, although it is more dense. The average of two determinations was nearly 0·000004—about the value for mercury. This is an interesting example of the rule to which no exceptions at moderate pressures have as yet been found: that liquids are more compressible than their solids.

*VII. The Surface Tension of Liquid Gallium.*

Mention has already been made, in brief extracts ("Carnegie Inst. Year Book," 1919, No. 18), of the work on the surface tension of gallium; the work is now to be described. For the present purpose, the flat-drop method often used for mercury (for example, Chwoison, *Lehrb. Phys.*, 1902, i., 602) is the most suitable, since, because of the property of adhering to glass possessed by gallium, the capillary-rise method could not be conveniently employed.

The flat-drop method consists in measuring the height between the greatest diameter of a large, flat drop resting on a horizontal surface and the highest level of the top of the drop, which must be large enough to have a perfectly flat surface in the middle. The drop, of course, must rest upon a surface which it does not "wet."

The mathematical expression for the computation of the surface tension reduces from a very complicated form to the simple equation $2\gamma = SA^2$, where $\gamma$ is the surface tension, $S$ the density of the substance at the temperature employed, and $A$ the height in millimetres above the maximum diameter.

The work of Laplace (Laplace, *Mec. Cel.*, 1845, iv., 538), Quincke (Quincke, *Pogg. Ann.*, 1858, cv., 38), and Meyer (Meyer, *Wied. Ann.*, 1894, liii., 845), may be merely mentioned. Heydweiller (Heydweiller, *Ann. Phys. Chem.*, 1898, lxv., 311; see also Gnadenwitz, 1899, lxvii., 467), like Quincke, called attention to the necessity of a large drop and further proved that the form of a solidified drop was of little use in determining the surface tension of a solid. Stöckle (Stöckle, *Wied. Ann.*, 1898, lxvi., 499) showed that after remaining for hours in contact with a gas, the liquid usually showed a smaller surface tension than at first, the final values agreeing essentially with those observed in a vacuum. Evidently, then, one must wait until constancy is attained.

In our own experiments the gallium of which the surface tension was to be determined was supported on a plane surface at the bottom of a small box immersed under the water of an accurate thermastat and fed with an atmosphere of pre carbon dioxide. The box was of iron about 15×8×10 cm. On its front side was cemented a small plane window of optical glass, and in the rear a somewhat larger window-pane was secured. Both were sealed into place by a watertight paste made from litharge and glycerine, protected by a thin coating of paraffin. The top of the metal container was closed with a piece of mica with a small hole for introducing the metal.

The plane surface employed for supporting the liquid metal was at first a block of paraffin, later a block of hard wood, and finally, when contamination from this substance was feared, a small block of gas carbon. Paraffin becoming somewhat softened at 30° adheres slightly to the gallium, and even hard wood was not wholly free from this difficulty, but carefully smoothed and polished gas carbon proved to be a wholly satisfactory support. The box was coated both inside and out with paraffin to preserve the gallium should it be accidentally displaced, and to prevent rusting and leaking. The carbon dioxide was passed through a U-tube immersed in the thermostat in order that it might enter at the constant temperature. The thermostat itself, consisting of a large square metal box, had a window of plane optical glass both in front and the rear. Very great care was taken to have the front pane and that of the container box vertical and exactly parallel in order that there might be no error from refraction. This was accomplished optically by measuring by means of a perfectly horizontal telescope (that of the cathetometer used later for measuring the height of a drop), the position of a distant spot of light (on a level with the telescope), as reflected in these glasses. The carbon dioxide employed was made from pure marble, and purified by a saturated solution of sodium hydrogen carbonate (the water having been boiled to free it from dissolved oxygen) and concentrated sulphuric acid. Air must be excluded wholly in order to prevent oxidation of the gallium. The purest sample of gallium employed was Sample E, already described; melting at 29·75° it must have been very nearly, if not quite, chemically pure.

Mercury also was measured, to serve as a check. Several samples were employed, the best having remained for sometime under sulphuric acid with agitation and also having been sprayed six times through a tower containing dilute nitric acid as well as finally through one containing water to remove the acid. The mercury was subsequently dried in a large evaporating dish, distilled in a partial vacuum, and filtered.

Before reading the height of the drop, the liquid metal was allowed to remain on its carefully levelled platform in the small thermostatted container with the perfectly vertical window until constancy was surely reached. No change was observed with gallium after 20 or 30 minutes, although usually at least an hour was allowed.

Mercury attained constancy even more promptly than gallium. The drop of the latter metal must be occasionally shaken and even stirred on top with a glass rod, introduced through a tube from the top, otherwise inconstant values, above the final constant one, are obtained. Perhaps a very thin quite invisible film of oxide sometimes formed and exerted a disturbing influence, in spite of the great pains taken to exclude oxygen. Of course, the drop must be perfectly dry and wholly free from acids.

The measurement of the height of the drop above the point of maximum diameter was usually made by locating the latter with the help of a small carbon-filament lamp on the level with the telescope. A brilliant point of light obviously appears on the desired level, and it is easy (especially if the aperture of the object glass of the telescope is much reduced in diameter) to measure the distance between this point of light and the flat top of the drop. The measurement was made by an accurate eye-piece micrometer which was standardised by moving the telescope exactly 1 mm. and counting the number of turns on the micrometer head necessary to bring the image back to the cross hair once more, or by actually measuring a metal rule in the thermostat at the same distance from the telescope as the drop of metal to be measured. Both methods gave essentially the same result for the standardisation of the micrometer.

In order to test the size of drop necessary to give the maximum height, drops of mercury varying from 1·6 to 23 g. in weight were measured, and of gallium varying from 3 g. to 10g. At least 15 g. of mercury (producing a flat drop with a diameter of 15 mm.) was needed to give an approximately constant value. 8 g. of gallium giving a drop of the same diameter was apparently enough to give nearly constant results with this less dense substance. Probably, in order to attain the highest accuracy, even larger drops should be used.

The final determinations for mercury and gallium follow. The large letters designate the purity of the samples according to the descriptions already given; the small subscript letters indicate different fillings and settings of the apparatus Each figure given consists of the average of 18 to 20 readings. Preliminary experiments with impure materials in which the various conditions of experimentation were developed, are omitted. All of the final results are given in each case.

TABLE IV.—*The Surface Tension of Mercury at* 30°.

Final Determinations.

| Setting | No. | Wt. sub. | Height drop mm. from max. diam. | Surface tension. Mg./Mm. | Resting on |
|---|---|---|---|---|---|
| *b* ... | 1 | 18·132 | 2·5501 | 43·97 | Wood |
| | 2 | 20·446 | 2·5532 | 44·08 | Wood |
| | 3 | 23·384 | 2·5548 | 44·12 | Wood |
| *c* ... | 1 | 17·968 | 2·5509 | 44·00 | Wood |
| | 2 | 21·762 | 2·5493 | 43·94 | Wood |
| | 3 | 27·837 | 2·5532 | 44·07 | Wood |
| *e* ... | 1 | 15·7 | 2·579 | 44·96 | Carbon |
| | 2 | 20·7 | 2·580 | 45·02 | Carbon |
| | 3 | 15·2 | 2·572 | 44·73 | Carbon |
| *f* ... | 1 | 12·31 | 2·542 | 43·69 | Carbon |
| | 2 | 16·84 | 2·544 | 43·74 | Carbon |
| *g* ... | 1 | 12·65 | 2·528 | 43·21 | Carbon |
| | 2 | 15·24 | 2·531 | 43·31 | Carbon |
| | | | | Av., 44·06 | |

*The Surface Tension of Gallium at* 30°.

Final Determinations.

| Sample and setting. | No. | Wt. ga. | Height drop mm. from max. diam. | $\gamma$ Mg./Mm. | Resting on |
|---|---|---|---|---|---|
| E*e* ... | 1 | 8·11 | 2·467 | 36·61 | Carbon |
| | 2 | 10·05 | 3·463 | 36·54 | Carbon |
| | 3 | 10·05 | 3·458 | 36·43 | Carbon |
| E*f* ... | 1 | 7·97 | 3·470 | 36·69 | Carbon |
| | 2 | 10·04 | 3·473 | 36·75 | Carbon |
| | 3 | 10·04 | 3·473 | 36·75 | Carbon |
| E*g* ... | 1 | 8·35 | 3·461 | 36·50 | Carbon |
| | 2 | 9·96 | 3·470 | 36·67 | Carbon |
| E*h* ... | 1 | 8·54 | 3·454 | 36·36 | Carbon |
| | 2 | 10·00 | 3·458 | 36·43 | Carbon |
| E*i* ... | 1 | 8·30 | 3·458 | 36·44 | Carbon |
| | 2 | 9·92 | 3·461 | 36·41 | Carbon |
| E*j* ... | 1 | 8·94 | 3·463 | 36·44 | Carbon |
| | 2 | 9·88 | 3·464 | 36·55 | Carbon |
| | | | Av., 36·54 | | |

The rather wide range in the case of mercury from 43·2 to 45·0 is greater than is desirable; it is doubtless due to the difficulty of adjusting all the optical requirements of the system to perfect uniformity. Since a great many different settings of the apparatus were made, it seems fair to conclude that the average has almost, if not quite, eliminated uncertainty from this source.

In the case of gallium the range is much smaller, probably because of increased experience and dexterity. The earlier experiments where the metal rested on paraffin and contained considerable indium were somewhat higher than the final ones made with purer substances and more satisfactory supports. These latter seem to leave little to be desired. In brief, then we find the surface tension of mercury at 30° to be 44·06 mg./mm. (which is very near that of Stöckle and other accurate experimenters), and that of liquid gallium to be 36·54 mg./mm. In terms of dynes/cm., the values become, respectively, 432·0 and 358·2, since $g=980·4$ in Cambridge. Thus the surface tension of liquid gallium is about five times that of water.

### VIII. *The Latent Heat of Fusion of Gallium.*

Berthelot determined the latent heat of fusion of gallium calorimetrically in the usual way, obtaining a value 19·08 calories per g. (Berthelot, *Compt. rend.*, 1878, lxxxvi., 786). We have used the somewhat preferable method, based upon the familiar equation of Clapeyron. The values in the equation $Q=T\ (V_l-V_s)\ dp/dT$ are easily determined with accuracy. In this equation, of course, $T$ represents the absolute temperature, $V_l-V_s$ the change of volume of a grm. of substance on melting, and $p$, pressure. Of course, since $Q$ is always positive (that is, heat is always absorbed on melting), an increase in volume on solidification necessitates a negative temperature coefficient. The experimentation is most conveniently carried out according to the method used by Demerliac (Demerliac, *ibid.*, 1896, cxxii., 1117; solidification necessitates a negative temperature pressure required to maintain equilibrium in a mixture of the solid and liquid phase at a fixed temperature.

Our apparatus consisted of a piezometer similar to that used in the compressibility experiments, but of only quarter the size, and with a narrower capillary. Within this piezometer the gallium

was contained in a small open test-tube protected from the mercury on top by an inert liquid. Neither the gallium nor the surrounding liquids need be weighed. The thermostat was arranged so that it could be adjusted quickly at any desired temperature over the range of 2° or 3°, and was provided with an adequate heating arrangement which could be regulated with great nicety. In detail the operations were as follows.

The piezometer (having been cleansed thoroughly and dried in a current of air) was partly filled with mercury and placed in a larger vessel which was evacuated in order to remove air. The little test-tube containing a cylinder of gallium (cast as before) was then placed in the piezometer, covered with either toluene or water, and again partly evacuated to remove air. After the piezometer had been completely filled with toluene (or water) and the stopper (without lubricant) placed in position, a portion of the gallium was melted, and sufficient mercury was placed in the side arm of the piezometer so as to make contact at the platinum point when equilibrium had been reached at the desired pressure. Since the piezometer was used at practically constant volume, the respective amounts of the two phases of gallium had to be adjusted to this volume by cautions melting or freezing, accomplished by temporarily altering either pressure or temperature.

The melting point of gallium was thus determined at various pressures between 200 and 450 megabars, by finding the pressure at which equilibrium was reached at a definite long-maintained temperature. The pressures were measured by the absolute gauge already mentioned, and the temperatures were referred exactly to the international hydrogen standard. The first three trials were rejected as merely preliminary, although essentially like the later ones. All the others are given in Table V.

TABLE V.—*Change of Melting Point with Pressure.*

| No. | Press in megabars. | Centigrade melting pt. | $\Delta P$. | $\Delta T$. | $\Delta P/\Delta T$. |
|---|---|---|---|---|---|
| (A) | 1·0 | 29·752 | — | — | — |
| 4 | 348·9 | 29·047 | 347·9 | —0·705 | —495 |
| 5 | 441·1 | 28·859 | 440·1 | —0·893 | —495 |
| 6 | 248·2 | 29·242 | 247·2 | —0·510 | —485 |
| 7 | 248·7 | 29·242 | 247·7 | —0·510 | —486 |
| 8 | 443·2 | 28·842 | 442·2 | —0·910 | —485 |
| 9 | 349·7 | 29·045 | 348·7 | —0·708 | —493 |
| | | Av. | 346 | | 490 |

These figures naturally fall into three groups when classified according to pressure, but it is evident upon comparing Experiments 5 and 8 at the highest pressure that the possible error of experimentation is as great as the total range in the values of $\Delta p/\Delta T$. Therefore these figures are not accurate enough (because of the comparatively small pressure range) to determine the change of $dp/dT$ with pressure. The best method of utilizing the results is to assume that their average applies to an average pressure, which must be taken as one-half of the average $\Delta p$, because $\Delta p/\Delta T$ is approximately equal to $dp/dT$ at about the average pressure involved in the range $\Delta p$.

(To be continued).

## BRITISH WEIGHTS AND MEASURES AND THE METRIC SYSTEM.*

FACED with a demand in certain quarters for the compulsory adoption in Great Britain of the Metric System, the Conjoint Board of Scientific Societies appointed a Committee to report on, not the theoretical advantages of the metric system which are indisputed, but the necessity of making it compulsory in this country for all intents and purposes. The British system of weights and meausures has grown unscientifically almost from prehistoric times, and the system itself, as well as the use which has been made of it is unnecessarily complex and wasteful of time and arithmetic. Its defects, indeed, are so obvious that there has been for many years strong propaganda in favour of its eradication. Bodies such as the Decimal Association have assumed that the metric system is undeniably superior, and have perhaps made light of the very real difficulties of a change. With every increase in complication of technical processes and the establishment of each new scientific industry, it has been almost natural to work in the metric system, which became so well known in our factories and machine shops during the war, that the time was undoubtedly favourable for a radical change in our units of measurement. Nevertheless, the Committee of the Conjoint Board, have, after long and careful consideration, confirmed the opinion expressed by Lord Balfour of Burleigh's Committee on commercial and industrial policy after the war—that it is not desirable to make changes compulsory; except perhaps in one or two special trades.

It cannot be denied, that many scientific men, as well as propagandists, consider this verdict thoroughly reactionary. It is therefore worth while to examine the question with some care. The Metric Committee point out in their preamble that the terms of reference—the advisability or otherwise of compulsory adoption—removed the question out of the purely scientific sphere, and made it necessary to consider the effects in common life as well as in technical manufactures and industries.

They point out the great distinction between measuring and making to measure, the latter being in ordinary life far more common than the former. In the greater part of common manufactures and small trades it is a case of making, often rather roughly, to a few given dimensions, or of weighing and measuring to one or other of a relatively few units. The British units are not well related, and especially they rarely have decimal relations, but such as they are they are well established and perfectly standardised. When reformers speak of confusion in British measures they must mean either complexity in relations, or confusion in use, for there is no confusion in the measures themselves, as there was between the different varieties of foot and pound in Central Europe little more than half-a-century ago, or as there is to-day in the varying values of the maund in different parts of India. The British pound and foot of unvarying standard are thoroughly established in the world, and no one has the slightest difficulty in knowing what they

* Note on the recent Report on compulsory adoption of the Metric System, by the Secretary of the Committee.

mean. But they lend themselves ill to calculation, owing to the fact that the various units are not inter-related decimally, which makes them totally unsuitable for any scientific work, and far from convenient in any technical work, such, for example, as the simple process of making up a photographic developer. All this is common ground. Nevertheless, the Committee came almost unanimously to the conclusion that for the ordinary purposes of life the metric system is not superior to the British system, since it does not lend itself readily to the ingrained habit of subdivision to halves and quarters, a habit which no decimal system is strong enough to conquer. Moreover, the Committee believe that the advocates of a change have not paid sufficient attention to material difficulties. The trouble of changing all the weights and measures in the country would be trifling compared with the difficulty of providing all the sacks, barrels, glasses, jars, boxes, &c., which would be required if all sales were to be made in metric weights and measures from a given date. They point out that the inconveniences of a change of system are felt in each individual transaction, and that the quantity dealt in is relatively unimportant. The retail trade in small quantities would feel the weight of the change. It does not appear to the Committee that any changes desirable in the units of weight in the foreign trade require the abolition of the avoirdupois pound as the unit of weight in the internal retail trade of the country. A change in the unit of length immediately interferes with all standard sizes and fits, which would inevitably be perpetuated almost indefinitely alongside the new. For reasons such as these, which are fully set out and discussed in their report, the Committee recommend that the British system of weights and measures be retained in general use in the United Kingdom, but that serious attention should be given to their decimalisation and to the elimination of those which do not lend themselves readily to this purpose. They suggest, for example, the abolition of the pole, furlong, and the league, and the limitation of the link and chain to use in the determination of area; the abolition of the square rod or perch and the rood, all areas of land being in acres and decimals, or in square feet. In the measures of weight they propose the abolition of the grain, drachm, stone, quarter, and cwt. of 112lb., and the complete abolition of apothecaries' weight. In the measures of capacity, they suggest the general use of the gallon, with the customary subdivision into quarts and pints for retail use; the abolition of the peck, bushel, quarter, chaldron, and barrel, and the substitution of measure by weight. Finally, and this recommendation is as important as any, they insist on a more sensible use of the remaining measures, by confining each statement of measure to one unit—75inches, for example, instead of 6 feet 3 inches—and the more extended use of the central and thousand-weight, which are already much employed in certain industries. In one trade only, that of drugs and fine chemicals, do the Committee recommend the immediate compulsory adoption of the metric system. They recognise to the full, however, the inadequacy of the British system in all scientific and technical processes, and they suggest that reform in these should be brought about gradually, by agreement on the part of Government Departments, large companies, and contractors, to issue specifications and invite tenders in the metric system.

A draft of the Committee's report was submitted to the Constituent Societies represented on the Conjoint Board and their criticisms are printed in full. The purely scientific societies, such as the Physical Society, the Faraday Society, and the Royal Society of Edinburgh, express strong dissent from the recommendation; while the technical societies, such as the Electrical Engineers, the Engineers and Shipbuilders in Scotland, the Institute of Metals, Mining Engineers, Naval Architects, and others, are in general agreement.

## PROCEEDINGS OF SOCIETIES.

### PHYSICAL SOCIETY.

*April* 8, 1921.

Mr. W. R. Cooper in the Chair.

The following papers were read:—

*"A New Registering Microphotometer."* By Dr. W. J. H. Moll, University of Utrecht.

A diminished image of a slit, on which the filament of a half-watt lamp is focussed, is projected by means of a microscope objective on the photographic plate or other object of which the absorption is to be measured. A second similar objective focusses an image of the slit, magnified up to its original size, on a second slit behind which is mounted a sensitive thermopile of the author's own design connected to an improved D'Arsonval galvanometer. By suitable gearing to an electromotor the photographic plate is given a slow motion at right angles to the beam of light, and at the same time a drum of photographic paper, on which the spot from the galvanometer is focussed, is caused to rotate at a suitable rate. A record is thus obtained of the density of the plate at different parts encountered by the beam of light. The arrangement is dead beat and so quick in response that intensity curves of close spectrum lines, Zeeman triplets, &c., are accurately recorded.

Discussion.

Mr. R. S. Whipple thought that the dead-beatness and quickness of the apparatus were unequalled. There was a beautiful feature of the records to which Dr. Moll had not referred; they showed the actual texture of the photographic plate as ripples on the base line. He believed the author was engaged in another research which would throw light on some important problems in connection with the blackening of photographic plates. It would be difficult for most of those present to imagine that the record of the Zeeman effect shown had been taken inside half-a-minute. It was a triumph of experimental skill.

Prof. Rankine said he had had the privilege of being about during the last few days when Dr. Moll and Prof. Ornstein had been erecting the apparatus. He had suggested that the instrument might be used to settle the question of the existence of the canals on Mars. In this connection Dr. Moll had told him that the eye saw many things which did not exist and missed many things

which did. An example which might be of interest to radiologists present was the case of an X-ray photo of a square hole in an opaque screen. It was frequently asserted that the intensity was greater at the edges of such a square than at the centre. The thermopile showed that this was wholly an illusion.

Mr. GUILD said he could only express the greatest admiration for the instrument they saw before them. He was particularly interested in the galvanometer. They had recently been installing radiometric apparatus in the Optics Department of the National Physical Laboratory, and were using a Paschen galvanometer. They were troubled so much with the zero changes due to stray magnetic fields from the adjacent electric railways and from sources within the laboratory that the advantages due to the sensitivity of the galvanometer were largely nullified. He looked forward with very great interest to the advent of Dr. Moll's thermopiles and galvanometers on the British market.

Dr. J. S. ANDERSON said he had had the pleasure of hearing Koch describing his microphotometer. He had thought the chief objection to Koch's instrument was the variability of the photo electric cell. The modern forms were much less variable, and probably the objection did not now hold to the same degree. Dr. Moll was, however, to be congratulated on so successfully employing the much more easily manipulated thermopile for the purpose.

Mr. C. R. DARLING thought the instrument would be readily adapted to form a recording radiation pyrometer.

Mr. F. E. SMITH said he would like to know how Dr. Moll had made such an excellent thermopile. Through the kindness of Mr. Whipple he had had the pleasure of working with one of them, and there was no question of its excellence, but he had not been able to see how it was made.

Dr. MOLL, in reply, said the secret of his thermopiles consisted of getting the junctions which received the radiation to be of very low heat capacity. With most thermopiles the bulk of the heat capacity was due to the solder at the junctions. His method of avoiding this was as follows: He took two thick plates of the metals to be used, constantin and manganin, and soldered them end to end, scraping off the excess of solder. The metals already joined in this way were then rolled out to the desired thinness, and cut into strips. In this way, strips only $2\mu$ thick were obtainable with no excess of solder at the junctions. The other junctions were made of large heat capacity to give constancy of temperature of the "cold" junctions.

As regards the galvanometer, the principal modification which he had introduced was to have the coil held by two strips of bronze in tension instead of suspending it by the upper strip in the usual way. This gave greatly improved constancy of zero.

*"Application of the Ionisation Spectrometer to the Determination of the Structure of Minute Crystals."* By. Sir W. H. BRAGG, F.R.S. (read in his absence by Dr. E. A. OWEN).

It is shown that crystals in the form of powder can be examined by the ionisation method. The powder is pasted on a flat surface and placed on the spectrometer table in the position ordinarily occupied by the face of a single crystal. A bulb current of 1 milliampere is sufficient to give satisfactory records.

DISCUSSION.

Mr. J. GUILD said that while listening to Dr. Owen, with the preceding Paper by Dr. Moll on improved thermo-electric meausurements still in his mind, he had been wondering whether the modern improvements in the methods of X-ray production and of radiometry had possibly brought us within reach of direct measurement of the energy of X-radiation. Using a sensitive thermopile with lead foil receiving plates, and a heavy discharge from a Coolidge tube, there might be sufficient energy stopped by the foil, although most of it would pass through, to give an indication on the galvanometer.

Prof. ORNSTEIN thought that insufficient energy would be stopped by the thermopile to produce any effect unless the lead was so thick that all the sensitivity of the pile would be destroyed.

*"A Balance Method of Using the Quadrant Electrometer for the Measurement of Power."* By Mr. HUBERT PARRY (read in his absence by the Secretary, Dr. D. OWEN).

A new method of using the quadrant electrometer for the measurement of electrical power is described. It involves the use of a potential-divider across the supply circuit, and a standard non-inductive resistance in series with the load. An ammeter and a voltmeter are employed to measure the supply voltage and the load current. An example of its application to determine the power-factor of condenser is quoted.

DISCUSSION.

Mr. C. C. PATERSON said he had worked for 10 to 15 years with electrometers for power measurements. He would like to see the method tried out more fully under varying conditions. With small power-factors one always had the result as the difference of two large terms when using the electrometer.

Another point was that the two voltages $V_1$ and $V_2$ were not in phase. Of course, $V_2$ was small, but it would surprise him to find that it was legitimate to add them as the author had done.

Dr. E. H. RAYNER said they had not yet tried the method at the National Physical Laboratory, but were certainly going to. He wondered if the difficulty mentioned in connection with small power-factors could not be overcome by connecting the needle to the mid-point of a large dividing resistance. There was always a danger, however, with small power-factors that the dividing resistance was not true as regards phase on account of the distribution of capacity.

Dr. A. RUSSELL congratulated the author. The method was novel to him. The old method was quite good for high voltages, but for low voltages he thought the author's method would be superior.

Dr. D. OWEN said: The author's Paper, of modest dimensions, contains an idea which promises to add decidedly to the value of the quadrant electrometer as used for the measurement of electrical power. The method, being a null one, possesses several advantages. In the first place, it makes it possible to utilise to the full the possession of an electrometer of the highest sensi-

bility attainable in virtue of mechanical design. Further, as the constant of the electrometer disappears from the expression for the power, the usual calibration experiment with non-inductive load becomes unnecessary.

In the form proposed, however, the method has one decided disadvantage, namely, that at low power-factors the power required was obtained as the difference of two separately determined quantities, each of which might be of much greater magnitude. This is so, indeed, in the very test chosen by the author for illustration, and the effect is evident in the considerable discrepancy between two successive tests on the same condenser.

Dr. Rayner has expressed the possibility of this source of error being overcome by connecting the needle to the mid-point of the non-induction resistance across the mains. This had occurred to me, and on trying it I found it to be the case. The adoption of this modification would not only eliminate the source of error occurring at low power-factors, but would simplify the expression for the power in the general case. Denoting by $V/n$ the voltage drawn from the potential-divider (denoted by $V_1$ by the author) the expression for the power supplied to the load becomes

$$W=\frac{V^2}{R}\cdot\frac{n-1}{n^2}$$

All that is required in a test now is to adjust the tapping-point on the potential-divider until the electrometer needle is at zero, and at that instant to read off $V$ on the voltmeter. $n$ may be observed at leisure, and the only remaining factor in the calculation of the power is the standard non-inductive resistance $R$.

## SOCIETY OF PUBLIC ANALYSTS.

*Ordinary Meeting April 6, 1921.*

Mr. Alfred Smetham, President, in the Chair.

Certificates were read for the first time in favour of Messrs. William Ellard Woolcott, Thomas Henry Pope, B.Sc., F.I.C..

A certificate was read for the second time in favour of Mr. Percy N. Mould.

The following were elected Members of the Society: Messrs. Jules Cofman-Nicoresti, Walter K. Fletcher, William Singleton, James Darnell Granger, Ph.D. (Berlin), F.I.C., Edward Bradford Maxted, Ph.D. (Berlin), B.Sc. (Lond.), Russell George Pelly, F.I.C., Francis George Henry Tate.

The following papers were read:—

"*The Estimation of Strychnine in Scale Preparations containing Quinine and other Cinchona Alkaloids.*" By T. F. Harvey, F.I.C., and S. Back.

The determination of strychnine in a scale preparation containing iron and quinine is a matter of some difficulty. Existing methods for the separation of these two alkaloids are discussed. Some of these are useless, whilst others give satisfactory results on pure alkaloids, but fail when applied to the somewhat altered alkaloidal residues obtained in the analysis of scale preparations. The method recommended by the authors, which has so far proved satisfactory in practice, is based upon two existing methods, viz: the tartrate method of Harrison and Gair, and the ferrocyanide method of Simmonds. The greater part of the quinine is directly precipitated as tartrate from an aqueous solution of the scales, an aliquot part of the filtrate being used for the extraction of the strychnine and residual quinine, the separation being then completed by the precipitation of the strychnine as ferrocyanide. Characteristic strychinine residues are mostly obtained. Check experiments were made. The occurrence of small quantities of other cinchona alkaloids is shown not to interfere, with the exception of quinine, the behaviour of which is described.

"*A Method for the Determination of the Acidity of Coloured Solutions.*" By J. L. Lizius, B.Sc., A.I.C.

The method consists of passing the approximately neutralised coloured solution through a filter paper previously treated with the indicator solution. Small quantities of standard alkali or acid are added to the solution, which is then refiltered, and this procedure continued until the filter paper gives the permanent colouration of the indicator.

"*The Action of Water on Lead.*" By J. C. Thresh, D.Sc., M.D., F.I.C.

The author referred to the conflicting views held with reference to this action, notwithstanding the large number of chemists who have attacked the subject. He, therefore, commenced *de novo*, and found that water free from dissolved oxygen had no action on lead, but if free oxygen be present, action begins instantly, and continues until all the oxygen is used up, the rate of action depending on the amount of oxygen present. He then proceeded to enter into theoretical explanations as to the chemistry of the reactions which take place.

"*A Colour Reaction for Aconite.*" By S. Mellaneh, M.D., D.P.H.

The author states that colour reactions at present known for aconite are really those of benzoic acid, and that colour reactions generally are seldom useful unless applied to pure alkaloids. He has devised a method which appears to be specific for aconite, and is very delicate, involving the use of potassium ferricyanide and formic acid. This the author considers very useful for medico-legal purposes, particularly in India, and it is applicable not only to the pure alkaloid, but also to the powdered root. He seeks confirmation of the test.

## NATIONAL ASSOCIATION OF INDUSTRIAL CHEMISTS.

At the Fourth Annual Meeting of the National Association of Industrial Chemsits held at Sheffield recently, and presided over by Mr. A. B. Searle, among other important business transacted was the reading of the General Secretary's report on the activities and progress of the Association during 1920, from which we note that:—

Although many difficulties were met with during the latter half of the year, chiefly as a result of the Coal Strike and the decline in trade, the N.A.I.C. came successfully through a period

which proved to be the most critical since its formation. At present there are nearly 1100 members on the register, and a slight gain in membership has been made: many other trade unions, on the contrary, were not so fortunate, and one union in particular has reported a loss of 50 per cent of its membership. The Secretary also states that there was a balance in hand at the end of the year, but this would not have been possible unless economy had been rigidly observed. The publication of a magazine by the Association was carefully considered by a committee, but was deferred on account of cost. The matter is not being lost sight of, however, as it is felt that such a publication would be of considerable value as a medium for keeping in touch with the members (especially those not attached to a Section), and also in making the Association's aims and objects more widely known. The amount of correspondence dealt with by Headquarters was particularly heavy, whilst reports on the Association's affairs have been published in the chief trade journals as occasion arose.

The President devoted much time in attending meetings of the various Sections, and in interviewing many of the individual members. He also gave lectures before the Sheffield Section, and his advice and assistance proved invaluable on numerous occasions. Indeed, the N.A.I.C. was very fortunate in being able to fill the vacancy created by Mr. Charlier's resignation from the Presidency so successfully. Full advantage was taken of the "Advice Bureau", and quite a number of members were helped with a variety of problems. Although much time and labour were spent in this way, the nature of the work does not permit of a detailed statement for publication. With regard to income tax rebates, it is interesting to note that a statement has been received from the Commissioners of Income Tax to the effect that, although rebates for damaged clothing, travelling expenses, scientific books, subscriptions, &c., cannot be granted indiscriminately to industrial chemists, members of the N.A.I.C. may put in a claim for such expenses if they are necessarily incurred in the course of their employment. The economic status of the members was always uppermost in the minds of the Association's officials, and a special committee was formed early in the year to consider and draw up a scale of minimum salaries. This very difficult and complex subject was tackled whole-heartedly by the committee, and eventually a scale was submitted to and approved by the National Council. A copy of the scale was then forwarded to all members with a request that any member receiving less than the minimum mentioned therein should communicate with the Secretary, who should then endeavour to secure an increase in salary. Although the Coal Strike and the slump in trade has interfered temporarily with this scheme, the results were satisfactory, and well over 100 members have received increases in salary. Even though these endeavours to obtain better pay were upset by unforesen circumstances, the experience gained goes to show that the Association has very good prospects of doing much better in this direction when trade is more normal. Another committee was also formed to discuss preliminaries with the British Association of Chemists in order to try and bring about an amalgamation. Several meetings have been held and many difficulties overcome. The negotiations are still proceeding. With regard to the employment bureau, there are now nine members on the register who are out of work, and 15 other members requiring a change of situation. Several members have secured situations with the Association's assistance, and two members have received considerable increases in salary. During the first eight months of the year, an average of one working day per week was involved in this service. There is undoubtedly a tremendous amount of work to be done in the interests of the industrial chemist, but first of all it is essential that every effort should be made to obtain a strong organisation, both numerically and financially, and one that is fully representative of the industrial chemists of Great Britain. It is possible that much headway may be made in this direction by amalgamation with the British Association of Chemists and possibly by affiliation with the "non-manual workers federation."

The Secretary also explained that it is imperative that every works chemist, both in his own interests and those of his fellow chemists, should belong to a trade union, and that it is his duty to make that union a strong one. Moreover, it is felt that there is a good chance of doing so because the works chemist, after the comparative safety which he has enjoyed during the last few years, now begins to realise that he must have his protective society like any other worker. Reference is then made to the work of the Local Sections which is both educational and social in character, and also to the invaluable support and assistance which has been rendered by the officers and councillors of those Sections.

All communications with reference to the N.A.I.C. should be addressed to the General Secretary, The White Building, Fitzalan Square, Sheffield.

## NOTICES OF BOOKS.

*Journal of Indian Industries and Labour.* Vol. I., Part I. 111 Pages+7 Pages of Illustrations.

All who are interested in Indian industrial questions will welcome the appearance of the new *Journal of Indian Industries and Labour*, the first issue of which has just been published by the Government of India. There is a distinct need for more publications of this kind, and it is stated that the Journal is to be supplemented by a series of bulletins dealing with special subjects. The Journal, as Sir Thomas Holland explains in a foreword, has been started on the unanimous request of Directors of Industries, and "in addition to its functions as a bond of union between those who are working towards similar ends in different provinces, it is intended as a medium for communicating to a wider public, within and outside India, information that will assist private enterprise." The first issue gives every reason to believe that it will fulfil the purposes for which it is intended.

Sir Ernest Low, who has had a long acquaintance with industry and with the Central Provinces, contributes an article on "The Possibilities of Industrial Development in the Central Pro-

vinces and Berar," in which, after a survey of the industrial assets of the Province and a suggestive discussion of the labour problem, he deals with such questions as Government assistance to industries and banking facilities.

Mr. N. M. Joshi contributes a frank and independent article on "Welfare Work in Bombay Cotton Mills," a subject he has made peculiarly his own. We are glad to observe that the Journal does not identify itself too closely with the official point of view, and that contributions from non-officials are invited.

The article on "Researches in Tanning and the Calcutta Research Tannery," by the Superintendent of the Tannery, Mr. B. M. Dass, gives a full account of the valuable work that the Tannery is performing. It is interesting to note that there is a vigourous competition for admission into the tannery, and a keen demand for the services of the men it trains. In pure reesarch too, the results attained fully justify the enterprise. The article is illustrated by plans and photographs, and should stimulate interest in the leather trade, which has boundless possibilities in India.

A research of a different type, but no less practical in its conclusion, is illustrated by Mr. Gadre's article on "Clove Oil from Clove Stems." Mr. Gadre is Industrial Chemist to the Government of the United Provinces. His experiments go to show that the extraction of clove oil from clove stems can be profitably undertaken in this country, and it is hoped that some enterprising firm will make the attempt.

Captain Frankau, in a short article on "The Gilt Wire and Tinsel Industry at Burhanpur, Central Provinces," deals with one of the oldest of the smaller skilled industries of India.

Minerals are represented by "Trade Notes on Bauxite," by Dr. J. Coggin Brown, of the Geological Survey, who is at present attached to the Office of the Indian Trade Commissioner in London. This article—which is one of a series on Indian minerals about to be published in bulletin form—should prove most useful. After a description of the appearance, distribution, and uses of bauxite, the author turns to trade particulars and deals with grades and specifications, the organisation of the markets, prices, and the sources of competing supply. There are some useful statistical tables, and in conclusion, a short discussion of the outlook for bauxite in India.

An interesting discussion of the industrial unrest in Bengal during 1920 is given in "Trade Disputes in Bengal," by the Director of Industries. The article is supplemented by useful statistics giving particulars of the different disputes, with the numbers of men involved, and of days work lost.

Mr. Fyfe, in the concluding article on "Industrial Education in Madras Presidency," gives a thoughtful discussion of the reasons for failure in the past, and the conditions necessary for success in this line in the future. It is satisfactory to note that the question is receiving attention, not merely from Government, but from local bodies and private firms, and Mr. Fyfe makes a number of suggestions which should not be ignored by those who are interested in this very vital question.

In addition to the articles, the journal contains Summaries of Industrial Intelligence for the different Provinces, and some miscellaneous notes. The Provincial summaries, are, unfortunately, not complete, but most of the leading provinces are represented. These summaries give a review of industrial activity throughout India, and of the part that Government is playing in industrial development.

The Journal is in a handy form, the print is clean, and the paper good. The price for a single issue is Rs. 1-8; the yearly subscription (for four issues) is Rs. 4-80. Applications for copies should be made to the Superintendent, Government Printing, India, Calcutta, or to agents for Government publications.

## NOTES.

CONJOINT BOARD OF SCIENTIFIC SOCIETIES.—The Executive Committee of the Conjoint Board of Scientific Societies state that at the General Meeting of the Board held in March last it was decided to discontinue the publication of the "Annual Calendar" and "Fortnightly Bulletin of Scientific Meetings (Diary of Scientific and Technical Societies)," owing to the heavy printing liabilities incurred.

CANADIAN NATIONAL EXHIBITION.—Applications for space from Canadian and American firms were reported in February last "to have been unprecedented for this time of year," and it would be advisable to forward applications at the earliest possible moment to the Secretary, Canadian National Exhibition, 38, King Street East, Toronto, Ontario, Canada.

BULGARIA.—According to a telegram which has been received in the Department of Overseas Trade from His Majesty's Minister at Sofia, the Bulgarian Ministry of Railways is calling for tenders, to be submitted by May 9 for 1000 tons of creosote and 50 tons of chloride of zinc. Further details are being forwarded, and will be available for inspection on receipt at the Department of Overseas Trade, 35, Old Queen Street,, Westminster, S.W.1. It is advisable that firms tendering should act either through their own agents in Bulgaria or through some merchant firm established there. The names of suitable firms are also available at the Department.

REVERSIBLE REACTIONS OF CARBON MONOXIDE ON IRON OXIDES.—Whether with ferric or ferrous oxide, as the latter is unstable below 580° C., only one equilibrium is possible below this temperature $Fe_3O_4+4CO \rightleftarrows 4CO_2+3Fe$. Above this temperature, on the contrary, there are two equilibriums before reaching iron. We have the Moissan processes :

$$Fe_3O_4+CO \rightleftarrows 3FeO+CO_2$$

$$FeO+CO \rightleftarrows CO_2+Fe$$

the three solid phases coexisting at 580° C. The composition of the gaseous phase could be followed with the refractometer. Constancy of temperature could be obtained by electric heating. Thus the curves of equilibrium can easily be formed.—*Comptes Rendus,* January 17, 1921.

Institute of Metals.—For the first time since its formation in 1908, the Institute of Metals will be paying in the autumn a return visit to a provincial city. This Meeting will be held in Birmingham on September 21-23, the first Autumn Meeting of the Institute having also been held in that city in November, 1908. Since then the membership of the Institute has grown from 200 to over 1350, so that the attendance at the first Birmingham Meeting, excellent though it was, should be quite eclipsed by that at the forthcoming Meeting. The arrangements for the September Meeting are in the hands of the Committee of the Birmingham Section of the Institute, of which Dr. H. W. Brownsdon, M.Sc. (Member of Council), is Chairman. The programme will include a reception by the Lord Mayor of Birmingham, visits to the University and works in the neighbourhood, as well as excursions in the locality. Persons desirous of attending the Birmingham Meeting as Members of the Institute should obtain the necessary application forms from the Secretary, Mr. G. Shaw Scott, M.Sc., the Institute of Metals, 36, Victoria Street, London, S.W.1, before April 20, when a Ballot for the election of members will take place. The subscriptions of members elected as a result of the forthcoming Ballot cover an extended period ending June 30, 1922. In addition to being able to attend the Birmingham Meeting, members elected as a result of the Ballot on April 20 will also have the privilege of being eligible to be present at the forthcoming Eleventh Annual May Lecture. This special Lecture, which is given each year by a distinguished metallurgist or engineer, is to be delivered at the House of the Institution of Mechanical Engineers, Storey's Gate, Westminster, S.W.1, on Wednesday, May 4, at 8 p.m., by Prof. T. Turner, M.Sc., A.R.S.M., the subject of the Lecture being "The Casting of Metals" Visitor's tickets are available for the use of non-members, and can be had on request being made to Mr. G. Shaw Scott, 36, Victoria Street, S.W.1.

Very Active Saccharose Preparations.—Treating 80 litres of crude yeast, during four days, at 28°- 25° C., with 100 of must and 50 of saccharose the percentage of saccharose is quintupled. The yeast thus treated, reduced by pressure to have 30·4 per cent dry weight, is subjected to autolysis at 15°- 16° C., in presence of toluol; then filtered. Saccharose is extracted with water from the residue of filtration and precipitated by alcohol. The solutions of this precipitate are yet a little turbid and probably contain proteinous matter. Treated with kaolin, and filtered, they are perfectly clear. Adsorption by kaolin causes loss of about 10 per cent. diastase. But activity per grm. of dry weight increases to about the same extent. The saccharose passes through the Chamberl and filter and collodion membranes; but dialysis improves the specific power of inversion and percentage of nitrogen in solution decreases.—*Bull. Soc. Chim. de France,* January 20, 1921.

Properties of Rubber.—According to O. de Vries, the general effect of steeping the coagulum in water is an extraction of substances from the serum, the result being a loss of weight of 0·2-0·4 per cent for crepe; 0·5-3 per cent for sheet; 0·2-3 per cent for non-rolled coagulum. The speed of vulcanisation is decreased. When steeping is prolonged there is a "maturation" with further loss of weight but an increase in speed of vulcanisation, so that the primitive retarding is decreased or transformed into an acceleration. Accelerators formed during "maturation" are only partially extracted by water. When, freshly rolled sheet rubber is steeped in water subsequent development of rustiness is not prevented, but greasiness is due to hygroscopic substances on the surface of the sheets, and tendency to development of moulds is prevented.—*Le Caoutchouc*, February 15, 1921.

## PAPERS RECEIVED.

"The Metallic Hydrides and the Action of Hydrogen on the Metals." By E. Tomkinson. A Paper supplementary to that of Mr. J. F. Corrigan, Chemical News, 1919, cxix., 259. Received April 18, 1921.

## New Patents.

This List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W.C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

9361—Blummer, E.—Process for the continual distillation of tars or oils. March 29th.
9436—Kime, F. P. J—Refining hydrocarbon oils, spirits, etc. March 30th.
9511—Kliva, Geo.—Manufacture of fatty acids from hydrocarbons March 30th.

*Specifications published this Week.*

142441—Strasser, A.—Process for deoidizing and refining copper.
137064—Darrasse Freres et Cie.—Process for the manufacture of valeric acid and of alkaline valerates.
139195—Gerber, V.—Manufacture of aluminium nitride.

*Abstract Published this Week.*

*Vanadium Oxides.*—Mr. P. A. Mackay of 70 Lombard Street, London, has recently been granted a Patent No 157555 for a process of treating vanadium ores with oleum. The solution is reduced for instance by sulphur, dioxide or hydrochloric acid, or a carbonaceous reducing agent may be added to liberate sulphur dioxide from the solution, or in case chlorine is present in the ore, an added reducing agent may be unnecessary. The solution is then diluted with water and the lead sulphate separated, leaving vanadyl sulphate in solution. The vanadyl sulphate may be neutralized to precipitate hypovanadic acid, or an oxidizing agent such as alkali permanganate may be added to obtain vanadic anhydride, or the solution may be electrolyzed in a diaphragm cell, when vanadic anhydride separated at the anode and a lower oxide at the cathode.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

## MEETINGS FOR THE WEEK

*Monday, April 25.*

Royal Society of Arts, 8. "Recent Applications of the Spectroscope and the Spectrophotometer to Science and Industry" by Dr. Samuel Judd Lewis.

*Tuesday, April 26.*

Royal Institution, 3. "Darwin's Theory of Man's Origin" by Prof. A. Keith.

*Wednesday, April 27.*

Royal Institution, 3. "Nationalisation and Bureaucracy" by Prof. H. S. Foxwell.
Royal Society of Arts, 8. "Research in the Wool Industry" by Sir James P. Hinchliffe.
Society of Chemical Industry, 7. (At Nottingham).

*Thursday, April 28.*
Institution of Electrical Engineers, 6.
Royal Society, 4.30. "The Vibrations of a Spinning Disc" by Prof. H. Lamb and R. V. Southwell. "The Hardness of solid Solutions" by Dr. W. Rosenhain "A Method of analysing Galvanometer Records" by W. Hartree and Prof. A. V. Hill. "A new Form of Wehnelt Interrupter" by F. H. Newman. "Some Experiments on Thermal Diffusion" by T. L. Ibbs. "Diffraction of Light incident at nearly the Critical Angle on the Boundary between two Media" by B. N. Chakravarty.

*Friday, April 29.*
Royal Institution, 9. "Advances in Astronomy" by Sir Frank W. Dyson.

*Saturday, April 30.*
Royal Institution, 3. "The Great Epoch of Exploration—Spain" by Dr. H. Y. Oldham.



## NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemical Apparatus, &c., for review or notice to be addressed to the EDITOR.

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# THE CHEMICAL NEWS.

VOL. CXXII., No. 3185.

## EDITORIAL.

THE recent Friday Evening Lecture at the Royal Institution, London, was delivered by Professor SIR JAMES WALKER, F.R.S., of Edinburgh University, on "Electrolysis and Electro-Synthesis."

After briefly explaining the meaning of the terms "Electrolysis" and Electro-synthesis," in which reference was made to the two men whose names will always be honoured in connection with the Royal Institutions—Davy and Faraday—the Professor gave a brief account of the electrolytic work of Davy, which led to the isolation of sodium and potassium. The synthesis of ethyl-malonated was successfully carried out upon the lecture table and also that of di-ethyl-succinate; this latter was performed in an apparatus furnished with two platinum electrodes, and the inflammability of the gas was demonstrated by blowing it into a soap solution and ignition. An identical procedure, using one electrode of platinum and the other of gold, gave rise to the production of oxygen, forming an explosive gas, which was demonstrated in the same way.

The lecture was well attended, and many prominent chemists were present.

It is usual to hold an Exhibition on these occasions, and opportunity was taken for a display of British-made chemical and other glassware. The apparatus shown was produced by James Powell & Sons (Whitefriars), Ltd., Wood Bros., of Barnsley, and John Moncreiff, of Perth, for whom Messrs. Powell are now acting as retail agents in London.

"Powell's" are one of the few remaining glassmakers in London, and they are shortly removing their glass-works to Wealdstone, Middlesex, where an up-to-date glass-making factory on a very large scale is being erected. Meanwhile the firm is extending its manufactures, and is producing scientific glassware, chemical and thermometer tubing, and many other articles.

The Exhibition included a fine collection of Art and cut-glass table-ware, Mosaic tablets, and glass for church decoration. A very fine window panel was shown in course of construction, and the method of painting upon glass with vitreous pigments was explained and demonstrated by one of their staff of artists. Great interest was shown by the chemists present in the chemical ware; beakers, flasks, boiling-tubes, and other necessities of the laboratory were exhibited, and appeared to be equal to the very best pre-war productions. This confirms the contention that the British glassworkers need only time to accustom themselves to the formation of the articles hitherto almost exclusively produced upon the Continent, to be able to construct them with equal excellence. Hard combustion tube, soft soda, and flint tube, enamel lens front, and coloured tubes of all kinds were shown.

The beakers and flasks were made by the firm of Wood Bros., of Barnsley, and John Moncreiff, of Perth, and the combination speaks well for the spirit of comradeship as one result of the war; British manufacturers are co-operating with one another, each firm specialising in one or other direction. In the case in point, the association of these three manufacturers will make it possible to purchase the products of any one of them in the show-rooms which Jas. Powell & Sons are shortly opening in Wigmore Street, W. It will be a distinct advantage to the users of scientific and medical glassware to obtain the very best English ware direct from the producers.

Another exhibit of the Company consisted in a large collection of lamp-blown articles, an industry which has recently been taken up by them; already at Wealdstone large workshops are in full swing, producing medical and other lamp-blown apparatus, the labour being almost exclusively carried out by young girls. Some of the articles are of a most intricate nature; atomisers, syringes, and ampoules of all descriptions were shown.

A still further exhibit was a large collection of really beautifully made artificial eyes. This craft needs very special enamels and other coloured glasses, and all the eyes shown were manufactured from "Whitefriars" material. The work is carried out by the firm of Wm. Halford, Senr., who for some generations have been engaged in the art, and it has been carried to a marvellous stage of perfection. The eyes when worn are absolutely indistinguishable from the living eye. Miss Carne, one of the proprietors, was present to explain the process of manufacture and exhibits.

Our chief object in describing this remarkable exhibition is to emphasise the fact that British glassmakers are actively preparing to make their country independent of foreign manufactures in the matter of glassware, and that technical difficulties have already been overcome. All that is needed is a temporary measure of protection during the early years of the industry, while labour is being trained. Furthermore it requires help to enable it to withstand the artificial conditions due to inequality of exchange, and the determined effort of our ex-enemies to throttle the British glass industry by "dumping," a process often encouraged by the middleman, who is, unfortunately, in many instances ready to allow prospects of immediate profit to outweigh all national considerations.

The importance of the glass industry cannot be too insistently brought before the country, and it is encouraging to see that the glassmakers at least are not only talking, but doing their best for the good of the nation.

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ROYAL INSTITUTION.—On Thursday, May 5, at 3 o'clock, Dr. C. S. Myers delivers the first of two lectures at the Royal Institution on "Psychological Studies: (1) the Localisation of Sound, and (2) the Appreciation of Music." On Saturday, May 7, Prof. E. C. C. Baly begins a course of two lectures on "Chemical Reaction." The Friday Evening Discourse on May 6 will be delivered by Sir Robert Robertson on "War Developments of Explosives," and on May 13 by Dr. W. Bateson on "The Determination of Sex."

## THEORY OF MOLECULAR REFRACTIONS.

By GERVAISE LEBAS, B.Sc.

### *Part I.*

SEVERAL systems of molecular refractions have at one time or another held the field. Those which are most noteworthy are the systems of Brühl and Eisenlöhr (for the Lorenz-Lorentz formula). The latter is an advance on that of Brühl, because it preserves a better relation between the atomic refractivities for the spectral lines $\alpha$, $\delta$, $\beta$, $\gamma$, and in several instances the atomic values are better calculated. It moreover embodies some important generalizations on the influence of substitution, especially of ethenoid links, and systems of unsaturated combinations. It also attributes a number of exaltations of the refractive value to the influence of the supplementary valencies. The system, however, labours under several important restrictions. One is—that the values for $CH_2$ are not always the most probable ones, and the value chosen for hydrogen, $H_\alpha$ 1·094, is not correct. The system is thus not adapted to a very close analysis of the data. The writer, who has traversed the whole field, endeavours to remedy these defects, and seeks to considerably augment the theory. Previous papers: *Trans. Faraday Soc.*, 1917, xiii., 1, Sept.; 1918, xii., 3; and another.

If it is desired to consider measurements for the different lines, it is usual to consider the magnitudes relative to those for $H_\alpha$ with differences (Dispersions). Comparisons can be made more satisfactorily, as follows. Eisenlöhr does so by calculating percentage differences

$$\frac{M_\gamma - M_\alpha}{M_\alpha} \times 100.$$

Thus, whilst these calculations involve relative dispersions, a better method seems to be to consider relative refractivities,

$$\frac{M_\delta}{M_\alpha},\ \frac{M_\beta}{M_\alpha},\ \frac{M_\gamma}{M_\alpha},$$

and to plot the ratios on a diagram against wave-length. The curves can then be compared. The refractivities for most substances vary very little in the region of $M_\alpha$ but the curves gradually become steeper as the wave-lengths diminish, until between $\beta$ ($483\mu\mu$) and $\gamma$ ($430\mu\mu$) there is a sharp upward bend till they become almost vertical.

The magnitude of the ordinates indicates the extent of what is known as unsaturation. When the compounds contain a complex unsaturated system, that is, one involving the conjugation of a number of unsaturated combinations, the ordinates at $H_\alpha$ may be very much increased.

#### *Relation between Refractivity and Valency.*

Traube has pointed out a very simple relation between the two:—

C 4×0·78; N 3×0·78; O 2×0·78.

The writer has recently calculated the atomic refractivity of combined fluorine, and finds that it varies between 0·67 and 0·84. There are sufficient indications that the numerical relation is not illusory, but is significant. If the molecular refractivities of carbon monoxide and dioxide be compared, the relation is found to be very exact:—

| C : O | Δ | O : C : O |
|---|---|---|
| 5·04 | 1·68 | 6·72 |
| $N_\alpha$O 1·68 | | $N_\alpha$2O 3·36 |
| 3·36 | | 3·36 |
| 4×0·84 | | |

Thus: $C^4$ 4×0·84; $O^2$ .2×0·84. It can also be shown that the augmentation for the addition $H_2O$ and HCl to —O— in dimethyl pyrone is 1·54 beyond the atomic refractivities. Since $H^\alpha$—O— 1·76, the value for $O^4$=1·76+1·54=3·30 (4×0·82). This result is similar to that for carbon.

The atomic refractivities for carbon and oxygen on the ordinary system is C 2·50; O 2·24. There is consequently a depression of the carbon below its value previously calculated —0·86, and an augmentation of oxygen by 0·56. From this point of view the former would be negatively, and the latter positively unsaturated. Thus the view of the unsaturation of a system depends upon how we approach the subject. Since negative anomalies are an undoubted fact on the ordinary system, this side of the question must be considered. It is too much to hope that the valency relation can be generally applied; it nevertheless affords an extension of our knowledge.

Since refractivities measure the space occupied by the electrical atom or molecule, these dots would represent small electrical charges (possibly electrons). The augmentations observed are related in such a way as to indicate small charges connected with the number of valencies concerned.

#### *The Relation of Anomalies for Substitution and Valency.*

| | | | | |
|---|---|---|---|---|
| | R—OH 1·48 | | R—O—R 1·62 | 1·76 |
| Δ | | +0·14 | | +0·14 |
| | R—SH 7·76 | | R—S—R 7·96 | R—S—R¹ 8·13 |
| | | +0·20 | | +0·37 |
| | R—SeH 10·88 | | R—Se—R 11·02 | |
| | | +0·14 | | |

The case of substitution by hydrogen in carbon by methyl or other alkyl groups leaves no doubt as to the origin of the augmentation

| | Δ |
|---|---|
| Split chains and substitution of ethenoid and acetylenic groups by $CH_3$ ... ... ... | +0·14 |
| Substitution of cycloparaffins... | >CH—$CH_2$+0·14 |
| Substitution of benzene ... ... | : C—$CH_3$+0·28 |

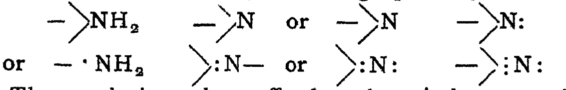
The augmentation 0·14 is characteristic of the methyl substitution, but the amount is doubled in benzene; half for the union with >CH— and half for the unsaturation. There is some indication that the augmentations are the result of accumulated electrical charges at the unions, for in some cases, especially in multiple unions, the augmentation vanishes as if short-circuiting took place.

*Nitrogen*.—A minimum value for nitrogen is $H^\alpha$ 2·12—2·20. This is found in elementary nitrogen $N_2$, nitric oxide N : O, and : N in some ring compounds. Taking this as the datum line, the augmentations for substituted nitrogen can be considered.

Amines.

| N. | NI. | NII. | | NIII. |
|---|---|---|---|---|
| 2·20 | 2·32 | 2·46 | 2·76 | 2·90 |
| | 2·20 | 2·20 | 2·20 | 2·20 |
| | +0·12 | 0·26 | 0·56 | 0·70 |
| | —— | 2×0·13 | 4×0·14 | 5×0·14 |

It is thus seen that the electrical charges depend not only on the number of substitutions, that is, on the bound valencies, but also in multiple substitutions on the supplementary valencies. The series can thus be represented graphically



These relations thus afford a clear indication of the connection between the augmentation for substitution and the fundamental or supplementary valencies. One has thus to consider two parts :—

A + ΔA

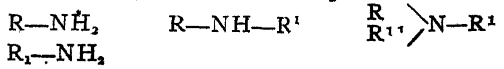
A a fundamental unsaturation of the atom ΔA is an augmentation which is due to substitution, and which must be added to the fundamental unsaturation to produce a new atomic value or considered separately. There might thus be a slope of potential from the nitrogen to the carbon, or the carbon to the nitrogen. The connection of a depressed value for multiple linked nitrogen is a very significant fact, and shows that multiple linking does not always involve an augmentation or positive anomaly, but a depression.

The anomalies indicate retardation of the right waves due to some cause. Since matter does this, and this is partly made up of electronic centres, the anomalies seem to be due to the presence of these in the edges of the atoms or more in the paths of the light waves than in the saturated compounds.

*Note.*—In considering the hydrocarbons from the valency point of view, gaseous methane possesses a refractivity of $M_\alpha$ | 6·72 8×0·84. The carbon atom thus shows an exaltation (on the old system) of 0·84, and the hydrogen 1·06—0·84=0·22, which, of course, is one-fourth of the total augmentation. The old system compromises matters by calculating from a mean condition.

One other consideration must be noted. Substances involving a number of alkyl radicles can be arranged according to the complexities of these radicles.

R—O —H R—O —R'
R—CO₂—H R—CO₂—R'



There will be disturbances differing with the position of the significant group, that is, with the complexity of the alkyl groups. The atomic refractivities are smallest when the significant group is terminal. It is required to accumulate data to such an extent as to be able to ascertain the disturbance throughout a series, and to arrange them as Dobriner did for the boiling-points and molecular volumes of the ethers, and Gartenmeister did for the carboxylic esters.

### *The Value of $CH_2$*

This subject has been frequently dealt with, but it does not seem to have been treated very scientifically. When a hydrocarbon becomes substituted by a reactive group X, the combination $CH_2$—X usually results in an augmentation for substitution. When X represents Cl, Br, I, OH, SH, &c., use is made of the ordinary values for the halogens, &c. These have been calculated from such homologous series.

The values for $CH_2$ throughout the series are found by means of the formula

$$H_\alpha\, CH_2 = \frac{M_\alpha\, C_n\, H_{2n+1}X - N_\alpha\, X}{n}$$

The curves as a rule show an initial depression, followed by a rise to the constant value for the series.

When the substituent is $CO_2H$, there is an initial augmentation for substitution. The ordinates which are large for the first member diminish greatly to the third, that is, as the alkyl groups neutralise the unsaturation. After this, the curve follows the previous one as the influence of the hydrocarbon element becomes preponderant.

In some cases there is a tendency to a maximum at some intermediate point, *e.g.*, in the case of the cyclo-paraffins. The maximum is at $C_6H_{12}$.

The disturbance for the combination $CH_2$—X, where it exists, is no doubt not only confined to the methylene group, but also to the substituent. It is possible that one or the other may be subject to a positive anomaly, whilst the other may be depressed. It has been assumed that X is constant throughout the series. Our knowledge is too limited to make a pronouncement on the subject, but this subject will be dealt with as it arises. It is, however, to a large extent a relative matter, and depends upon our datum line. The point is, are we to refer the exaltation to R or to X? It is becoming the practice to indicate such a disturbance by a thickened line $CH_2$━X. The writer proceeds differently, and indicates the unsaturation by a single, double, or triple dot. Since refractions measure the space occupied by the electrical atom or molecule, these dots would represent electrical charges (possibly electrons), and also would occupy space. The augmentation observed are relative in such a way that the connection with linkages (bound valencies) and the supplementary valencies is evident.

The relative values for $CH_2$ are always the same.

| α | δ | β | γ |
|---|---|---|---|
| — | 1·0046 | 1·0155 | 1·0245 |

Three main series are useful in calculations :—

| | | | | |
|---|---|---|---|---|
| (a) | 4·58 | 4·60 | 4·65 | 4·692 |
| (b) | 4·60 | 4·621 | 4·671 | 4·713 |
| (c) | 4·612 | 4·633 | 4·683 | 4·725 |

The constants for hydrogen are :—

| | | | |
|---|---|---|---|
| 1·06 | 1·065 | 1·076 | 1·086 |

The constants for carbon can be found by difference.

The first series is useful for all open chain compounds up to a complexity, $C_{10}$ say. The second is as a general mean value. The third is especially useful for the cyclo-paraffins, aromatic and terpenoid compounds. It must be stated that these differences are small as compared with those for general unsaturation.

### *The Activation of Supplementary Valencies.*

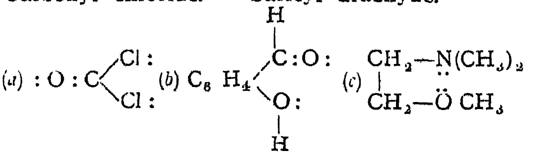
The case of nitrogen has just been studied. The halogens also show similar relations. Comparison is made between their refractivities under ordinary circumstances and when combined with unsaturated carbon.

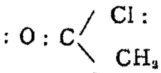
| | $CH_2$—X | Δ | :C—X |
|---|---|---|---|
| F .... | 0·67 | 0·17 | 0·84 |
| Cl .. .. .. | 5·96 | 0·22 | 6·18 |
| Br .. ... . | 8·79 | 0·23 | 9·02 |
| I .. ... ... | 13·87 | 0·25 | 14·12 |

There is a slight progressive increase in the value of Δ from fluorine to iodine. The graphic representation of the second series is : C—Cl : for example. The augmentation is due to the stimulating effect of the unsaturated carbon. The only principle to guide one in this case is analogy. There is nothing to show that the augmentation is not represented by : C—Cl. It may, however, be noted that the value of Δ approximates to 2×0·14

The activation of the supplementary valencies may be due to the influence of unsaturated atoms other than carbon.

Carbonyl chloride. Salicyl aldehyde.



| (a) | | (b) | (c) |
|---|---|---|---|
| 0·70 | M ... ... | 34·03 | 0·52 |
| 3×0·23 | Phenol ... | 27·75 | 4×0·13 |
| acetyl chloride | Benzaldehyde | 31·77 | |
|  | | 59·52 | |
| | *Less* $C_6H_6$ ... | 25·93 | |
| 0·46 | Calc. ... ... | 33·59 | |
| 2×0·23 | Obs. ... ... | 34·03 | |
| | | 0·44 | |
| | | 2×0·22 | |

Many cases are found among the xanthates and other compounds. It is evidently not always necessary for the unsaturated atoms to be connected by unsaturated carbon, although this is usually the case. This augmentation is distinguished from the ordinary anomaly. The above cases seem to show clearly that it is the supplementary valencies which are activated. The ordinary linking is only susceptible to an augmentation of 0·14 or 0·28 at most. It is noted (1) that atoms of high atomic weight are more likely to activate one another than those of lower; (2) the effects are greater if the atoms are united by an unsaturated group than a saturated one.

Peroxides :—

—O—O— 2×1·76

Disulphides :—

| | | |
|---|---|---|
| Et—S—S—Et | 36·33 | |
| | 20·44 | |
| | 15·89 | |
| | 15·92 | 2×7·96 |

Diselenides :—

| | | |
|---|---|---|
| $C_3H_7$—Se—Se—$C_3H_7$ | | |
| | 32·38 | |
| | 29·60 | $(C_3H_7)_2$Se gives Se 11·12 |
| | 22·78 | |
| | 22·24 | |
| | 0·54 | |
| | 2× 0·27 | |

Sulphur may, however, be much more activated owing to combination with unsaturated groups to form a series (*vide ante*).

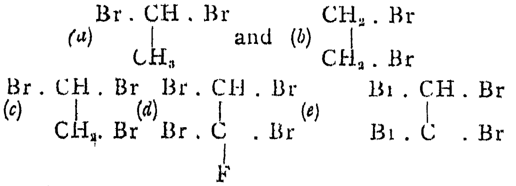
Karvonln has found from a comparison of the acid chlorides, bromides, and iodides, and other halogen series, that the disturbances augment from chlorine to iodine :—Cl > Br > I.

It is found that phosphorus, arsenic, and antimony are difficult to deal with owing to unlooked for augmentations. A detailed investigation of substances containing these and other heavy atoms is proceeding in various directions, and the conditions are much more complicated than in hydrocarbons.

The question of the influence of substitution is specially dealt with under definite circumstances—geometrical isomerism, keto enol charge, &c. One case may be mentioned at this point, viz. :—

### *The Influence of Massed and Distributed Substitutions.*

If comparisons be made between



(a) Average Br 9·07; (b) 8·82; (c) 8·84; (d) 8·80: (e) 8·61.

The following are instructive :—

| | $(CH_3)_3C.CH_2Br$ | | $(CH_3)_3.CCHBr$ |
|---|---|---|---|
| Mδ | 31·83 | Δ | 38·58 |
| | | 6·75 | |
| | | 1·06 | |
| | | 7·81 | |
| $C_5H_{11}$ | 24·06 | | 23·00 |
| Br | 8·83 | | 17·66 |
| E | 32·89 | | 40·66 |
| M | 31·83 | | 38·58 |
| | Δ —1·06 | | — 2·08 |

Δ Br —1·05

This depression is remarkable and belongs to a class of compounds distinguished by *negative* anomalies, as already shown for furfurane and thiophene.

$C(CH_3)_2.(CH_2Br)_2$ is normal.

The conditions (a) + anomaly; (b) normal; (c) —ve anomaly thus await exact explanation.

The unbalanced condition results in a higher refractivity than the balanced or symmetrical one. The compound $CBr_3.CBr_3$ would doubtless show a larger depression still.

A comparison between corresponding chlorides, bromides, and iodides would show disturbance of magnitude depending on the halogen

Chlorides < bromides < iodides.

[Electrons are regarded as material nuclei + central and accumulative, —ve kinetic and energy dissipating. They are thus unsaturated centres.]

## FURTHER STUDIES CONCERNING GALLIUM.

### ITS ELECTROLYTIC BEHAVIOUR, PURIFICATION, MELTING POINT, DENSITY, COEFFICIENT OF EXPANSION, COMPRESSIBILITY, SURFACE TENSION, AND LATENT HEAT OF FUSION.*

By THEODORE W. RICHARDS and SYLVES ER BOYER.

(Concluded from p. 185.)

ONE other point must be taken into account before applying the Clapeyron equation, namely, the change of $V_l - V_s$ with change of pressure. Since the solid is less compressible than the liquid, although more bulky, this change of volume on melting will increase as the pressure increases. Ordinarily this correction has been left out of account in the application of this equation, but it was properly heeded by Bridgman in his paper on "Water, Liquid and Solid, under Pressure" (P. W. Bridgman, *Proc. Am. Acad.*, 1912, xlvii., 471). The case of water is, of course, similar to that of gallium. Since the cubic compressibility of the liquid per megabar is about 0·000004 and that of the solid about half as great, the correction to be applied to the volume change over 173 megabars will be 0·00034 cc. per cc. of the metal, or 0·00006 per g. The value for $V_l - V$ at the atmospheric pressure is —0·00531. Hence at a pressure of 173 atmospheres it must be —0·00537.

We have now all the data needed by the Clapeyron equation:

$$Q = T\,(V_l - V_s)\,dp/dT$$
$$= 302{\cdot}5\,(-0{\cdot}00537)\,(-490)$$
$$= 79{\cdot}6 \text{ joules}$$
$$= 19{\cdot}04 \text{ cal. per g. (at 173 megabars pressure).}$$

This value is very nearly the same as Berthelot's 19·08, but since the latent heat of melting of gallium, like that of ice, probably changes with pressure, the identity is perhaps not as close as it appears to be. Nevertheless, the two figures cannot be widely discrepant, even applying the as yet unknown correction for pressure. Probably $dp/dT$ also changes with pressure, as Bridgman found in the case of ice; and if so, it probably changes in such a direction as to counteract, or perhaps, even reverse the effect of the change in $V_l - V_s$. The decision concerning this matter must be left to future investigations. Unless a much wider pressure range is employed, the measurements of both $\Delta P$ and $\Delta T$ will have to be made with the utmost accuracy in order to solve the problem.

The value of $\Delta P/\Delta T$ given in the foregoing table is equivalent to a change in the melting point of 0·00204° per megabar, or nearly 0·00207° per atmosphere. (P. W. Bridgman, in a research of which a description is now in the press, found the nearly equal quantity 0·00203° per kg./cm². with a small quantity of our gallium. The megabar is 0·987 atmosphere or 1·02 kg./cm².). This change in the melting point is more than twice that produced upon ice under the same conditions.

We are indebted to the Carnegie Institution of Washington, as well as to an anonymous fund, for generous support in this investigation, and also to Mr. F. G. McCutcheon, of the Bartlesville Zinc Company, for his courteous presentation of part of the material used as the source of gallium.

* From the *Journal of the American Chemical Society*, February, 1921.

*Summary.*

This paper contains a description of experiments leading to the following conclusions.

I. (*a*) The observed single electrode potential of gallium was not easily reproducible at a constant value. It reached in maximum only about —0·30 volt in 0·1 *N* solution (if the calomel electrode is taken as +0·56 volt), apparently placing gallium between indium and zinc in the electrochemical series.

(*b*) On the other hand, gallium is distinctly more difficult to precipitate electrolytically from acid solutions than zinc. According to repeated experiments, gallium might be expected from this behaviour to have a single electrode potential of at least —0·7. It can be precipitated in weakly acid solutions if sufficient current density is employed, however.

(*c*) A possible explanation of this apparent inconsistency is to ascribe a mild degree of passivity to gallium—an explanation borne out by the fact that this metal when pure precipitates copper only very slowly from its solutions.

II. After preliminary purification by electrolysis, which easily eliminates indium and many other metals, pure gallium was freed from zinc by ignition in a high vacuum and especially by crystallisation, giving material of constant melting point.

III. The melting point of gallium was found by two methods to be 29·75° C. on the international hydrogen scale.

IV. The density of the purest gallium was found to be 5·904 and that of liquid gallium 6·095, both at the melting point. The expansion on solidification (0·00531 cc. per g.) was proved not to be due to impurities.

V. The cubic coefficient of expansion of solid gallium was found to be about 0·000055. Hence the density of the solid at 20° is 5·907, and its atomic volume 11·85.

VI. The compressibility of solid gallium was found to be 0·0000020, and that of the liquid about twice as great.

VII. The surface tension of liquid gallium in carbon dioxide at 30° was found to be 36·54 mg./mm. In control experiments with the same apparatus, that of mercury at the same temperature was found to be 44·06.

VIII. The latent heat of fusion calculated from the Clapeyron equation and the change of melting point with pressure was found to be 19·04 calories per g. at 173 megabars pressure; that is, the melting point is lowered 0·00207° by the increase o fpressure of one atmosphere.

## SILICIC ACID.

By VICTOR LENHER.

THE relations of silica and water in the so-called silicic acids and the silica gels, and the mechanics of the solution of silica by water, are problems which for many years have received a great deal of though by chemists and geologists. The following experiments, which have been extended over a period of years, have been carried out largely to obtain a better knowledge of the relations that silica and water bear to each other.

*Effect of Fine Grinding on Silica.**

The starting material was Ottawa sand containing over 99 per cent. of silica. It was ground for 400 hours by means of large rounded pieces of quartz in an Abbe ball mill. This period represented the actual time of grinding, although the attendant operations and the grinding were conducted daily for several months. Great care had to be taken to prevent caking. The average fineness of the ground material was no more at the end of 400 hours than it had been at the end of 350 hours; and by evaporating in platinum with hydrofluoric and sulphuric acids it was found to contain 98·72 per cent., showing that a slight amount of impurities had been introduced from the grinding apparatus. Measurements were made of the size of the ground silica particles by placing samples on a glass slide, moistening with water, and covering with a cover glass. The samples were then examined with a microscope with a calibrated ocular and showed that 85 per cent. of the material had a diameter of less than 0·004 mm, while 15 per cent. was between 0·004 and 0·016 mm. in diameter.

This finely-divided material was shaken up with 500 cc. of conductivity water and allowed to settle at room temperature in tall, glass-stoppered cylinders. W. Machaelis in a paper read before the German Portland Cement Manufacturers on March 9, 1909, states that quartz reduced to an impalpable powder by prolonged grinding becomes so active that boiling with water will convert it into colloidal hydrated silicic acid. When the heavier particles had completely subsided, and the supernatant liquid appeared homogeneous but not completely transparent, the liquid was examined by evaporation of 100 cc. portions to dryness in a platinum dish and the residue volatilized with hydrofluoric and sulphuric acids. The results of this procedure indicate that in from two to three weeks silica to the extent of 0·028 to 0·032 g. per litre remains permanently in solution.

When first shaken with water, the ground silica forms a mechanical suspension and a large part of the suspended matter settles quickly. In a short time the finer particles form strata which at the end of about 10 days disappear, and at the end of 15 days the solution is stable.

*Colloidal Character of the Silica in Water.*

When viewed with the ultramicroscope the fine particles which remained suspended in the water after the ground silica had been shaken and the whole allowed to settle for several weeks, showed a rapid Brownian movement.

When a powerful beam of light was passed through the liquid in a beaker the exhibited Tyndall effect was produced.

These experiments show that if quartz is ground sufficiently long, it can be so finely divided that it will go into colloidal condition when treated with water.

From the rate that the particular material worked with settled out from water, it would seem that up to two weeks the whole is a more or less coarse suspension which slowly settles and finally leaves a stable colloid.

*With G. G. Town.

*Experiments on Fine Grinding of Orthoclase**

Carefully selected orthoclase was ground for 388 hours in an Abbe ball mill. The mill was opened daily and the caked material dislodged. This material was shaken up with water and allowed to settle in the same way as has been described with quartz. An additional experiment was conducted by shaking the finely ground feldspar with alcohol. After settling, both the alcohol liquid and the water liquid of the orthoclase showed the Brownian movement when observed with the ultramicroscope and also gave the Tyndall effect. The water suspension was filtered through a Chamberlain F. filter, and was then optically empty, but when filtered through an acid-hardened filter-paper (Schleicher and Schüll, No. 602), it showed particles which exhibited the Brownian movement. This should fix the size of the particles as between $4\mu$ and $1{\cdot}3\mu$.

Samples of this extremely finely powdered feldspar which had been suspended in alcohol for a short time were decanted, and the alcohol evaporated off and heated in an autoclave with water. One g. portions of this material, heated with 100 cc. of water in a platinum dish, for three hours at 168°, corresponding to 50 kg. steam pressure, showed an alkalinity against 0·1 *N* hydrochloric acid equivalent to less than 0·5 per cent. of $K_2O$, indicating that only a small portion of the feldspar had actually gone into true solution.

*Action of Water at Elevated Temperatures on Quartz.*

As is known to those who have worked with water in glass and siliceous material of various kinds at high temperatures and pressures gelatinisation takes place. From the many experiments with silica and water which have been conducted in this laboratory, it would seem that the first thing which takes place when silica is wet is hydration. Some of the silica then passes into solution and if allowed to remain in contact with water will finally reach the solution equilibrium shown by Lenher and Merrill (Lenher and Merrill, *Journ. Am. Chem. Soc.*, 1917, xxxix., 2630). Along with this process of hydration and true solution that portion of the silica which is sufficiently fine goes into the colloidal condition. When the temperature is raised this hydration takes place so rapidly that it can be readily followed.

At 400° in the sealed high-pressure bombs of Morey, water will slowly gelatinise all of the fused quartz or silica ware on the market to-day. At 500° water will slowly cause the gelatinisation of transparent quartz crystals. The resulting silica gels differ widely in character, depending on the temperature and pressure, and also on the original quartz used. Some of the gels when air-dried go to a loose, finely-divided powder; others dry into concentric layers and into fairly adhering compact plates.

Some recent experiments made by G. R. Shaw show that certain fused quartz tubes, when heated to about 500° with water in a bomb, on cooling give evidence of recrystallisation on the sides of the tubes. Numerous fragments were noted which under the polarising microscope showed

*With G. G. Town.

optical activity and also showed hexagonal structure.

Some preliminary experiments made by O. J. Noer with the finely-ground quartz prepared by G. G. Town seemed at first sight to be very significant. At 100° in a bomb, water hydrates this ground material in a manner which appeared to be definite. A number of experiments seemed to show by *analysis* that metasilicic acid, $H_2SiO_3$, was formed, the results of various experiments agreeing to within a few hundredths of 1 per cent, and agreeing exactly with the theoretical percentage requirements of the formula $H_2SiO_3$. However, the material which to the naked eye appeared homogeneous, when examined under a polarising microscope proved to be far from homogeneous. In reality it consisted of the broken fragments of the original quartz, interspersed with masses of gelatinous silica; it was, therefore, not metasilicic acid, but a physical mixture of silica gel and quartz. This hydrated material when allowed to dry spontaneously in the air hardened to a compact coherent mass which in texture, hardness, and general appearance much resembled quartzite.

The action of water at various temperatures and pressures on silica and on silica gels has been studied by Walter T. Schrenk in considerable detail. Several hundred experiments were made in a Morey bomb at temperatures which varied in the individual experiments from 300° to 600°, and the lengths of time of the experiments varied from 8 hours to 312 hours. The experimental difficulties to be overcome in work of this character have been almost insurmountable. While thus far it has been impossible to obtain the quantitative measurements that are desirable, it can be said in general that the extremely finely ground quartz previously described hydrates at 300° to 450° in presence of excess of water to a gel containing 15 to 18 per cent of water. On the other hand, silica gels made by the dialysis of the sodium silicate-hydrochloric acid mixture and containing 2·33 per cent of silica, the remainder being chlorine-free water, when heated from 300° to 600° in the bomb with great excess of water, lose water, and in from 8 to 312 hours yield a product containing approximately 20 to 30 per cent of silica and 70 to 80 per cent of water.

*Effect of Pressure on Silica Gels.**

The salts of orthosilicic acid, $H_4SiO_4$, and of metasilicic acid, $H_2SiO_3$, are found among some of our best-known silicate minerals. The free acids themselves are compounds that have plenty of analogues in the fourth group of the periodic system of which silicon is a member. Our common sodium silicate itself is a substance whose composition depends entirely on the quantities of reacting substances used in its original formation.

A very suggestive method described for the formation of orthosilicic acid is that of Norton and Roth (Norton and Roth, *Jour. Am. Chem. Soc.*, 1897, xix., 832). Their method of producing gelatinous silicic acid by passing silicon tetrafluoride into water is considered by them to be a method particularly desirable in order to obtain the material free from non-volatile foreign matter. They washed the gelatinous mass with water on a cloth filter and allowed it to drain a short time, after which the water was removed by ether or benzene. The washed acid was then squeezed in a vise and an orthosilicic acid of constant composition, reported as a definite body.

In our studies with silica these particular experiments seemed of sufficient promise to follow out in more detail. The particular points which looked attractive were a study of the effects of various and measured pressures on silica gels. If silica gels can be dehydrated by pressure from the condition of a high degree of hydration to the definite hydrate of the formula $H_4SiO_4$, it would seem that by using various pressures it should be possible to plot a curve showing the relation between pressure applied and the water remaining with the silica.

For the preparations of gelatinous silica it was most convenient for us to hydrolyse pure silicon tetrachloride. The gel was washed with water until free from chlorides, after which the excess of water was removed by squeezing the product between cloths by hand. The gel at this stage contained between 80 and 90 per cent of water and was preserved in a glass-stoppered bottle for use.

In place of the vise used by Norton and Roth, who could in this device obtain only about 100 kg. pressure per square inch, a Riehle testing machine was used. By means of a machine of this kind it is possible to obtain a compression of 45,400 kg. to the square inch, and to apply any particular pressure up to 45,400 kg. that is desirable.

In the first experiments, comparative low pressures were used. 230 kg. pressure, which is probably what a good vise would give, gave a mass which contained 77·7 per cent of water; 340 kg., 71 to 73 per cent of water; 454 kg., 68·5 to 71 per cent of water; 680 kg., 50 to 67·5 per cent of water; 900 kg., 46·5 to 53·5 per cent water; 1800 kg., 51 to 52 per cent water. In these experiments the gels were pressed between sheets of Whatman's filter paper, but at pressures of 2300 kg. and upwards, the adherence of the product to the paper became so pronounced that it was found necessary to use a canvas filter cloth as the medium to absorb the water. With 4540 kg. pressure, the water retained by the silica was from 57 to 60 per cent. At pressures from 4540 to 13,600 kg., various combinations of canvas filter cloth and hardened filter paper with copper foil gaskets were used. The water content then dropped down to 44·5 per cent at both 9000 and 13,600 kg. At 13,600 kg. two sheets of heavy rubber were also tried as a support for the gel, but 55 per cent of water still remained. In another series of experiments a laboratory diamond steel mortar was used at pressures of 11,600 and 13,600 kg. with the results that about 30 per cent. of water remained. The results obtained with the diamond steel mortar were so encouraging that it was decided to use tool steel plates.

Two carefully faced round steel plates 100 mm. by 12·5 mm. were used and as the water was squeezed out of the gel, the free water was removed by means of filter paper. The amounts of water remaining with the silica was of the same general order as with the other devices employed. The product in each case, after being pressed, looked, in the ordinary sense of the word, dry. Using the tool steel plates a pressure of 44,600 kg. was attained, yielding a product which retained 34 to 35 per cent water.

*With Andrew J. Snyder

In order to continue the experiments at still higher pressures, two special chrome-nickel-steel plates, kindly furnished us by Dr. Geo. W. Sargent, of the crucible Steel Company of America, were carefully machined in such a manner that their contact surfaces were parallel to within 0·00508 mm. From the contact surface to the outer edge of the discs they were slightly bevelled to take up the flow of the steel at very high pressures. These plates withstood the pressure of 272,700 kg. very well, and the results obtained were fairly constant. A Tinius Olsen hydraulic press was used to obtain this high pressure. The product obtained showed a water content of 12·3 to 12·9 per cent, which closely approximates the ratio of one molecules of water to two of silica, corresponding to the formula $H_2Si_2O_5$. The final product was a white amorphous powder, which under the microscope showed no crystalline structure.

A number of the gels, after being pressed to 272,700 kg., were transferred to desiccators and allowed to stand for various periods of time. The material which was approximately two molecules of silica to one of water actually contained 12·5 per cent water, and in two months desiccation over phosphorus pentoxide lost 5·75 per cent of water, but still retained 6·75 per cent; while the material which was dried further over calcium chloride retained at the end of two months 9·24 per cent of water. Longer desiccation would doubtless remove more water.

From the results obtained by submitting gelatinous silica to the successively high pressures studied, should it be possible to press a silica gel more strongly than has been done, it seems probable that more and more water would be removed as the pressure increased.

From the observations made by Lenher and Merrill (*loc. cit.*), it is obvious that silica possesses a very definite solubility in water.

When quartz is ground sufficiently fine, pure water alone will cause it to go into the colloidal state as has been verified by actually finding it to be a colloid. Additional evidence of the fact that fine grinding alone can sub-divide a substance so finely that water will cause it to go into colloidal form, is afforded by the fact that orthoclase when ground extremely fine goes into the colloidal form in exactly the same general manner as does silica itself.

The action of water on silica is therefore that of a solvent, to produce the silica gel, and to cause it to go into the colloidal form. The more finely divided the silica the more rapid is the action. This action of water on silica with the subsequent hydration is accelerated by heat and with water under high pressures, such as are obtained in the steel bombs, the hydration of large-sized quartz crystals or even fused quartz can be readily followed.

The silicic acids themselves are purely hypothetical. While their salts form our common silicate minerals, the acids in free condition have never been prepared. The so-called "silicic acid" and the gels which are so common should therefore be regarded as corresponding to the general formula $XSiO_2YH_2O$ in which the quantities of water and silica can vary from a true solution of silica in water, successively through the highly hydrated gels which pressure alone will convert from a water content of nearly 98 per cent to a silica which contains only a few per cent of water. —*Journal of the American Chemical Society*, March, 1921.

## PROCEEDINGS OF SOCIETIES.

### FARADAY SOCIETY.

*Tuesday, March* 22, 1921.

Prof. Alfred W. Porter, F.R.S., President, in the Chair.

The President delivered his Presidential Address entitled "Some Aspects of the Scientific Work of the late Lord Rayleigh." He indicated that Rayleigh's work was of many varieties. The experimental part could be divided into that requiring elaborate apparatus and laborious application such as in the case of the determination of the ohm, and investigations in which the apparatus was of the simplest kind. The latter was a type of investigation in which Rayleigh specially delighted. His mathematical work was always looking forward to its applications. Illustrations were given of the great use he made of the method of dimensions when problems (especially those in hydrodynamics) cannot be yet solved in any other way. His theoretic work on intrinsic pressure was outlined and contrasted with more recent work of the Dutch School of Physicists. Finally, his mentality was further characterised by references to his excursions into problems dealt with by the Society of Physical Research. His position was summed up by saying that although Rayleigh founded no school yet he so advanced knowledge of physics in all its branches as to stand out as one of the leaders in scientific achievement.

Papers were also read by Mr. S. Field on the "Electrolytic Recovery of Zinc"; by Prof. Alexander Findlay and Mr. V. H. Williams on the "Electrolytic Reduction of Glucose"; and by Mr. W. E. Hughes on "Iron Deposits."

## CORRESPONDENCE.

### COAL TAR FOR CAIRO.

*To the Editor of the Chemical News.*

Sir,—I beg to inform you that a cable has been received in this department from the British Commercial Agent in Egypt (Mr. E. Homan Mulock), stating that tenders are invited by May 15 for the supply of 1000 tons of coal tar to the Roads Office, Tanzim Department, Cairo, to be delivered between July 1 and October 15. Alternative prices can be quoted for British Standard Specification No. 2 or any coal-gas tar suitable for road spraying. The conditions of tender are those usual in contracts made by the Egyptian Government, and it will be observed that tenders will only be accepted from firms having agents or representatives resident in Egypt. It is understood that no special form of tender is required, though a sample of the tar offered must be submitted. In view of the conditions of this contract, United Kingdom firms, without representation in Egypt,

may, it is thought, care to avail themselves of the services of a firm with an Egyptian branch, through which tenders could be submitted, and I shall be pleased to forward you particulars on receipt of a request to that effect.—I am, &c.,

L. N. Barker,
for Comptroller-General.

Department of Overseas rade,
April 21, 1921.

## HEBREW UNIVERSITY AT JERUSALEM.

*To the Editor of the Chemical News.*

Sir,—At the Third Annual Conference of the Inter-University Jewish Federation held at Oriel College, Oxford, on August 3, 1920, it was unanimously resolved, in response to a request of the Zionist Organisation, to render every possible assistance to all efforts on behalf of the Hebrew University at Jerusalem. The most urgent need at the present juncture is an immediate and abundant supply of books for the Jerusalem University Library. We can conceive no cause more precious and commendable than the full development and firm consolidation of the intellectual and spiritual resources of the Jewish National Home. To this end books are the first requisite. In a scarcity of books the mind of a people is denied free expansion and healthy growth. To Jews, with their love of learning, the want of books is most distressing. In Palestine, unfortunately, there is a real book famine, and even with help from all over the world, it will need a great effort to build up the present University Library of about 40,000 volumes, into an up-to-date library worthy of the Jewish University.

Serious works dealing with all branches of knowledge, standard works of fiction in any language, and more especially books which will be of use to University students are needed. Books on Hebraica, Judaica, and Semitica, mathematics, physics, chemistry, microbiology, and medical research are, however, the most urgently called for, as the first departments of the University that are to be opened will deal in research in these subjects. Books on law, economics, history, and philosophy will also be much appreciated. Sets of scientific journals, transactions of learned societies, official reports and other publications and works and pamphlets of permanent value are especially required; good text-books of established repute will also be useful.

Considering that this is an important step towards a spiritual revival of Palestine, and that our credit as an enlightened people is at stake, we appeal to your readers to send all the books they can spare as a free-will offering to those who will treasure them in Palestine. A single book will be welcome; but it is hoped that donors will send as many as they can. Gifts of books may be sent either direct to "The University Library, Jerusalem," or to the Hon. Secretary, Mr. D. B. Stanhill, B.Sc., F.I.C., 75, Great Russell Street, London, W.C.1, who will, if necessary, arrange for the collection of the books. An artistically designed book-plate, the generous work of Mrs. L. Pilichowski (Lena Pillico), will permanently record the names of the donors.—We are, &c.,

S. Alexander, *Chairman*,
Israel M. Sieff, *Treasurer*,
D. B. Stanhill, *Hon. Secretary*,
Harry Dagul, *Chairman, I.U.J.F.*

## NOTES.

Board of Trade Announcement.—The Board of Trade announce that by notice published in the *London Gazette* of April 8, the provisions of Section 11 of the Aliens' Restriction (Amendment) Act, 1919, which imposes restrictions on the acquisition by former enemy aliens of certain kinds of property, have been applied to the following industries, namely, the manufacture of synthetic organic dyestuffs, colours, or colouring matters, and the manufacture of organic intermediate products used in the manufacture of synthetic organic dyestuffs, colours, or colouring matters. The effect of this is to make it unlawful for any former enemy alien to acquire either in his own name or in the name of a trustee, any interest in the industries in question, or any share, or interest in a share, in a company registered in the United Kingdom which carries on the industries.

In the *Astrophysical Journal* for March an important paper appears by R. A. Millikan, I. S. Bowen, and R. A. Sawyer, on the "Extreme Ultraviolet Spectrum of Carbon, Iron, and Nickel." By the use of a special form of grating and a vacuum spectrograph, the authors have succeeded in obtaining records of iron lines from $\lambda$ 2152·9 to $\lambda$ 271·5 AU, carbon from $\lambda$ 1931·1 to $\lambda$ 360·5, and nickel from $\lambda$ 1859·7 to $\lambda$ 731·0.

British-American Alliance.—With a view to further cementing a happy relationship established some time ago with organisations in America and Canada, propagating similar objects to their own, namely, the improvement of relations between employers and employed, the Executive Committee of the Industrial League and Council recently decided to send a delegation to America for the purpose of conveying fraternal greetings, but primarily to study economic conditons and ascertain the possible channels through the medium of which a revival of trade can be stimulated. The idea has received the cordial approbation of large organisations of employers and employed on the other side of the Atlantic, and amongst the messages which have been received by Mr. John Ames, General Secretary of the Industrial League and Council, is the following cablegram: "Civic Federation will warmly welcome delegates of Industrial League. Congratulations upon happy turn in your great industrial conflict.—(Signed) Ralph M. Easley." It is evident from the last sentence that both employers and employed in America have closely watched developments in the Coal struggle. The Federation in question is the National Civic Federation of America, of which Mr. Samuel Gompers, President of the American Federation of Labour, is a vice-president, and the organisation embraces within its ranks all the big employers and representatives of labour in the United States. Mr. L. J. P. Benn, C.B.E., Hon. Treasurer, and Mr. Frank Elliott, a member of the Executive Committee, are the delegates from the League. They are sailing on the 23rd inst., and while in the States it is their intention to devote particular attention to the problem of the readjustment of wages in view of the falling prices, and the steps which are being taken to re-establish overseas trade. An interesting tour has been mapped out which will include all the big indus-

trial centres between New York and Kansas and Chicago and Quebec. The Industrial League entertains high hopes that as a result of the visit, and the establishment of more intimate relations with American manufacturers and employers, a great step forward will be accomplished towards the revival of trade.

Tenders Invited for Australia.—H.M. Senior Trade Commissioner in Australia has forwarded copies of specifications, conditions, and forms of tender in connection with calls for tenders by the Postmaster-General's Department for the supply and delivery of (1) ironwork, including couplings, piping, bolts, rings, &c. (Schedule No. 704); (2) 29,500 porous cells, No. 1 size to specification (Schedule No. 1685); (3) 20½ tons ammonium chloride (Schedule No. 1683). Sealed tenders on the proper forms will be received by the Deputy Postmaster-General, Perth, Western Australia, up to May 25 in the case of (1), and by the Deputy Postmaster-General, Melbourne, Victoria, up to May 31 in the case of (2) and (3). Local representation is essential, and as the time for the receipt of tenders is limited, it will be necessary for firms tendering to instruct their local agents by cable. Copies of the specifications in connection with the above tenders may be consulted by British firms interested at the Department of Overseas Trade (Room 59), 35, Old Queen Street, Westminster, S.W.1.

The Casting of Metals.—Prof. T. Turner, M.Sc., A.R.S.N.I., of Birmingham University, will deliver the Eleventh Annual Lecture at the Institute of Metals on this subject on Wednesday, May 4, at 8 p.m. The meeting will be at the Rooms of the Institution of Mechanical Engineers, Storey's Gate, Westminster, S.W.1. Coffee and light refreshments will be provided at the conclusion of the lecture.

Revival in Manufacture of Linoleum.—The actual penury of linseed oil, colophony, Kauri gum, jute, and cork, as also their high prices, constitute an obstacle to revival of the linoleum industry. By utilising all the accumulated waste, German works were able to resume manufacture, but this resource will only provide for a brief period, the quantity of waste materials being insignificant. Moreover, these works are equipped for a somewhat great production, and all reduction necessarily involves a loss in working. Linseed oil is the most important raw material, but considering its cost other oils are sought after. Whale and shark oil, prices of which are moderate, can, by direct oxidation, be made suitable for linoleum, combined with linseed oil and small quantities of wood oil. By insufflattion of air, as in methods for rapid oxidation, these oils lose their bad odour. By subsequent fusion with colophony, the odour completely disappears, so that the finished products are quite free from a fish oil odour. These oils can also be polymerised in presence of free fatty acids and magnesia; then converted into linoleum, compounds yielding oxygen being added. Other oils may also be employed, viz., perilla oil, soja, grape pips, hemp, walnut, poppy, and sunflower oils, &c. As a substitute for linoxin the pitch of stearin works can be utilised, or colophony can be replaced by rubber resins. These last have the advantage of not forming combinations with zinc, oxide, magnesia, or lime, differently to colophony, which forms very hard products with them, which make linoleum brittle. To avoid these inconveniences, when these polymerised oils are employed with magnesia, it is well to previously etherise the colophony with glycerin. Hardening is less to be feared with demi-siccative oils. Cork can be replaced by peat or sawdust, and jute by paper tissues.—*Chimie et Industrie*, January, 1921.

Variation in the Rotary Power of Tartaric Acid.—Continuing the study of this variation, which is different to that previously given, M. R. de Mallemant examines the action of solutions of metallic chlorides and nitrates. The fall increases in the series of alkaline metals and decreases in the order Sr, Ba, Mg, Zn.—*Comptes Rendus*, January 17, 1921.

## New Patents.

This List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

10508—Farberke vorm. Meister, Lucius & Bruning.—Manufacture of sodialk-ylaminoethylaracy oxybutyric acid esters. April 9th.

9927-9928—Hadden, P.—Process for converting organic acids into esters. April 4th.

10315—Lo, Monaco, D.—Chemical fertilizers. April 7th.

10493—Passmore, F. W.—Manufacture of magnesium salts. April 6th.

*Specifications published this Week.*

137288—Thibault, J. A.—Method of converting metallic lead into oxides.

156080—Wacker, Ges, Elektrochemische Industrie, Dr. A.—Manufacture of dichlorethylene.

*Abstract Published this Week.*

*Lead Sulphate.*—Mr. P. A. Mackay of 70, Lombard Street London, has been granted a Patent No. 157554 for an improved process of obtaining lead sulphate by treating the sulphide ores free from zinc, preferably galena and oleum, which may be in excess without any external heating. The reaction vessel should be insulated to avoid loss of heat. When an excess of oleum is employed, the sulphate is precipitated by dilution with water, and the excess acid may be recovered.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

## MEETINGS FOR THE WEEK

*Monday, May 2.*

Royal Institution, 5. (Annual Meeting).
Society of Chemical Industry, 8. (At London).

*Tuesday, May 3.*

Royal Institution, 3. "Darwin's Theory of Man's Origin" by Prof A. Keith.
Röntgen Society, 8.15.
Royal Society of Arts, 4.30.

*Wednesday, May 4.*

Royal Society of Arts, 4.30.
Institute of Metals, 8.
Society of Public Analysts, 8. "Detection and Estimation of Illipé Nut Fat used as a substitute for Cocoa Butter" by Francis G. H. Tate and John W. Pooley. "Notes and Demonstration on Apparatus for determining Hydrogen ion concentration" by G. W Monier Williams. "A Note on the Oil of Oats" by Ernest Paul. "Estimation of Potassium in presence of Sodium, Magnesium, Sulphates and Phosphates" by H. Atkinson.

*Thursday, May 5.*

Royal Institution, 3. "Psychological Studies—The Localisation of Sound" by Dr. C. S. Myers.
Institution of Electrical Engineers, 6.
Chemical Society, 8.

*Friday, May 6.*

Royal Institution, 9. "War Developments of Explosives" by Sir Robert Robertson.
Society of Chemical Industry, 7. (At Manchester).

*Saturday, May 7.*

Royal Institution, 3. "Chemical Reaction" by Prof. E. C. C. Baly.



## NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemical Apparatus, &c., for review or notice to be addressed to the EDITOR.

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THE CHEMICAL NEWS.
VOL. CXXII., No. 3186.

## THE COLOUR AND MOLECULAR FORMULA OF WATER AND ICE.

By E. TOMKINSON.

### *Part I.*

In connection with Prof. W. D. Bancroft's recent paper on this subject, the following notes may be of interest (see Chemical News, 1919, cxviii., 197, 208, 222, 233, 248, 254; and 1921, cxxii., 9, 34). (*Note.*—Rayleigh's work on He and Ar is noticed in the Chemical News, 1920, cxxi., 248, *c.f. Nature,* 1920, p. 584).

Prof. W. Spring, at the 5th International Congress of Hydrology, Climatology, and Medical Geology, Liège, October, 1898, delivered an address on the colours of natural waters, in which he states that, when pure water has a very slight cloudiness, due to the presence of finely-divided nearly white or colourless particles. Even if these are absolutely colourless, as in the case of very finely-divided rock crystal, a yellow tint is given to the water, which, *together with the natural blue proper to the water itself,* produces a green colour, as in the cases of the Lakes of Neuchatel and of Constance (*c.f.* other explanations, Bancroft, *loc. cit.*). The usually green colour of certain lakes occasionally becomes absolutely colourless, which is due to the washing into the lakes of a fine mud of a reddish tint (iron oxide), which neutralises the green colour, rendering it for the time being perfectly colourless.

A rather different aspect of the question was brought forward by the work of Threlfall (Richard Threlfall, *Nature,* 1899, lix., 461), thus: "During a recent voyage by the Messageries steamer "Polynesien," I was permitted, through the kindness of Commandant Bullard, to erect a tube 736 cm. long against the rail of the after-deck, and to pass through it a continuous stream of water from the ship's salt-water service. The water was taken in well forward, and at a depth of two or three metres, and consequently was not soiled by the passage of the ship. I made a series of observations with the apparatus described, matching the colour of the sea-water by making mixtures of definite substances and using these mixtures to fill a tube 18 cm. long, placed alongside the water tube.

"Both tubes were illuminated by diffused daylight reflected from a white screen, and by the aid of diaphragms, etc., it was arranged so that the angular area of the visible part of the screen was the same whether observed through one tube or the other. Observations were made every day on the voyage from Sydney to Marseilles, but owing to the uncertainty arising from the contamination of the water by the varnish with which the interior of the tube was protected, it is useless to comment on most of the results obtained, except in so far as they give a means of easily reproducing the exact tint of pure sea-water as seen through a column 736 cm. long.

"Make up the following solution: water 500 cc., soluble Prussian blue, 0·001 grm., saturated lime-water, just precipitated by the smallest excess of bicarbonate of soda, 5 cc. This mixture when when viewed through a tube 18 cm. long, will show with considerable precision the colour of a sample of water from the Mediterranean, lat. 36 deg 24min. N., long. 17 deg. 51 min E. (of Paris). By using various lengths of tubes I found that when a match has once been made, it can be preserved (within the limits tested) by increasing the amount of Prussian blue proportionally to the length of the column of water under consideration.

"In these tests I made use of tubes 183 cm. long, which could be mounted in series; the relation held as the number of tubes was increased from two to five. I consider that it would be worth while for a series of measurements to be made systematically by this method, and therefore mention that the tubes must be of black porcelain or glass; the water must be pumped by the observer's private pump (which must be worked off the electric service), and must give a pressure large enough for a Berkefield filter. The colour of daylight is also too variable on the deck of a ship protected by awnings, and a form of artificial illumination should be employed.

"In making the colour matches, it is best to arrange to look down the two tubes simultaneously, using one eye for each tube. By slight squinting, it is easy to get the sensation of two patches of colour on the screen side by side.

"The majority of the samples of water examined by me took 25 per cent less blue to match them than the sample quoted, and when the water was soiled by the tube, and perhaps at other times, it was necessary to add an amount of picric acid to a large proportion of the Prussian blue, and of course, giving a green solution. The transparency of the water is estimated by the amount of precipitated chalk it is necessary to add. At the same time, I am not sure that the loss of light observed, and requiring the addition to the match, is produced by turbidity. It is just as likely that the absorption spectrum of water is crossed by a faint but uniform band from end to end. In this case, a black liquid might be added to make the match, but I do not know of one which is anything like black in very dilute solution; of definite materials the best was the aniline dye sold under the name of steel-grey, but it was very distinctly purple.

"The water on the West and South-West coast of Western Australia is perhaps more interesting than any I have seen, for it is very green indeed, and very clear; so much so as to raise a doubt of the adequacy of Aitken's explanation (*Proc. Roy. Soc. Edin.*, 1882, ii., 472; see also Bancroft, *loc. cit.*), especially as the sand looks white rather than yellow. It is just possible that the sea may in certain places dissolve a sufficiency of yellow colouring matter from living or dead sea-weed to account for the green tint. All the observations I made convinced me that the possible scattering of light by very fine particles in suspension has got nothing to do with the colour of the sea-water."

In reply to the above (*Nature,* 1899, lix., 509), Aitken points out that he never stated that the yellow particles are the exclusive cause of the greenness in sea-waters, and concludes (p. 510): "As the waters of most of our rivers are yellowish brown, it is probable that it is the addition of this yellowish water to sea-water that makes the seas

surrounding our islands of a greenish colour"; but such an explanation obviously does not apply in the case of the Australian water described by Threlfall.

In Threlfall's paper, reference is made to the absorption spectrum of water. Hartley and Huntington (*Phil. Trans.*, 1879, clxx., 257), using the spark spectrum of an alloy of tin, lead, cadmium, and bismuth, found that water is quite diactinic transmitting all the rays as far as $\lambda = 2000$ Å.U. On the other hand, Colley (A. R. Colley, *Journ. Russ. Phys. Chem. Soc.*, xxxviii., 431; xxxix., 210) found that absorption bands occur in the optical and electrical spectra of water.

Water vapour, however, shows absorption in the infra-red; for example, the "a" 7165 absorption band, no bands occur for wave lengths of less than $\lambda = 5884$ Å.U. It was by the "a" band that the presence of water-vapour was detected on Mars (see Rolston, *Nature*, 1907, lxxvii., 442; Slipher, *ibid.*, 497; Lowell, *ibid.*, 503, 606; Campbell, *ibid.*, lxxxiv., 317).

A dark line or band in the spectrum of water has been reported (T. W. Backhouse, *Nature*, 1910, lxxxiv., 530) at $\lambda = 6000$ Å.U. approximately, occurring in bluish-green fresh water and in sea-water. This line would tend to make water blue, but its effect is masked by strong general absorption in the whole of the red and orange beyond this dark line. In sea-water, this general absorption was found to extend more feebly to the D line of the solar spectrum, and even to the dry air band $\delta$. The deep green of Lago Maggiore gave an almost identical line. This line was not found in the water of Lake Geneva, noted for its deep blueness, but the general absorption at the red end of the spectrum was very striking. Backhouse states that the bluest water is at Lago di Gonda, and the Blane See, near Handersteg. At the former place, the blue colour of the water was slightly tinged with green, but was often bluer than the bluest sky.

Sir E. Ray Lankester (*Nature*, 1910, lxxxiii., 68) drew attention to the beautiful light-blue colour of the water in storage tanks which had been treated for hardness by Clark's process, the colour being independent of the condition of the sky, and visible at (almost) any angle of vision. He also noticed that the white porcelain of a bath appeared distinctly blue with a layer of water 20in. high in strong sunlight, the intensity of colour varying with the movement of the water in waves or ripples.

It has been shown (H. T. Barnes, *Nature*, 1910, lxxxiii., 188) that the rich blue colour of the hard clear ice at Glacier, B.C. persists even with small pieces of the ice; and surface ice, which has been slowly formed by conduction, and taken out of the St. Lawrence River, shows the same effect—but the block loses its colour after long exposure to light, and very rapidly in sunlight. Coloured sediment and air-cavities detract from the colour. Barnes attributed this colour to a "real absorption effect due to the large molecular aggregates, which absorb the long rays, and not a "blue-sky" effect. Sea-water is particularly blue, and here we have the added effect of salt molecules (in addition to which the water of the sea is very clear). W. H. Skerzer (Smithsonian Report, 1907) showed that the blue colour of the water and ice of the Canadian Rockies is a real absorption effect, the blue colour being increased by the presence of minute white sediment but not by coloured sediment." He refers to the analogy of the beautiful blue colour of liquid air as soon as most of the nitrogen has boiled away (due to the formation of complex oxygen molecules), and notes that the variations of specific heat, density, viscosity, and compressibility of water with temperature are due to gradual diminution of the molecular aggregates. It will be noted that this suggestion is in agreement with that advanced by J. Duclaux and Mme. E. Wollmann (*Journ. Physique*, 1912, (v), ii., 263—see Chemical News, 1921, cxxii., 9, 34).

W. N. Hartley (*Nature*, 1910, lxxxiii., 487) found that optically pure water cannot be prepared by distillation, even by first distilling with acid permanganate, and then re-distilling from a copper vessel into a receiver placed in a hydrogen atmosphere (which latter provides an optically pure atmosphere), but pure (optically) water was prepared by Tyndall by melting clear block ice in a vacuum, and this water was blue when viewed through a tube 3ft. in length. Prof. Hartley stated that it is only possible to observe the beautiful blue colour of the water at Fairy Loch beside Loch Lomond, being where it wells up from a fissure in the rock and passes over a vein of milk-white quartzite. In another instance, the blue colour was only observed when a white object was placed in the water. Hartley's explanation is that the blue is wholly due to absorption of rays of complementary colour; because, if not, the reflection of the blue rays by suspended fine particles should be seen against a dark ground on looking into the water, but this was found not to be the case. Against this we know that the light escaping reflection has a reddish-golden colour. He concludes: "In a hazy atmosphere when the sun is low and we look towards it we seen the golden colour; in the opposite direction we see the blue opalescence. The white light from the sky traversed the (last-mentioned) water in two directions to the bottom, and then, by reflection, back again, and it is safe to say that these two opposite colours would neutralise each other." (The water when undisturbed on the surface was almost invisible, but the bottom of the pool was composed of red stone.—E.T.).

A very interesting account of observations made on the "Challenger" and at other times is given by J. Y. Buchanan (*Nature*, 1910, lxxxiv., 87). He states that the green colour of the Antarctic water is due to the abundance of diatoms, and to a greater extent, to the excretions of animals for the subsistence of which the diatoms furnish the ultimate food supply. He says that the three colours of the ocean are ultramarine and indigo and the above green, and very properly notes that for the correct observation of the colour the greatest amount of light must reach the eye after passing through the water, and the least after reflection. By observation through the "screw-well" of the "Challenger," he was convinced that the water contained in its own mass sufficient colour to account for all that was perceived. As a result of experiments in the mid-Pacific, he concluded that the length of the uninterrupted column of (sea) water which transmits the more intense colour (pure but pale ultramarine) must be many times greater than 25 fathoms. He showed that the green colour of the sea-water at Mogador is

due to altered chlorophyll (see also W. N. Hartley, "Deep-Sea Chlorophyll," *Proc. Roy Soc. Edin.*, 1885, xiii, 130); and similarly for the water from Valparaiso to San Francisco.

Prof. Bancroft (*loc. cit.*) referred to the possible analogy between the colour of the blue sky and that of water. Lord Rayleigh has recently shown that the former is due to scattering of light by suspended particles (Friday Evening Discourse, Royal Institution, May 8, 1920; *Nature*, 1920, cv., 584). He has shown that light from the blue sky is polarised (when examined at right angles to the sun), just as is the blue light produced by scattering by particles of sulphur formed by addition of acid to a solution of sodium thiosulphate, the laterally scattered light in the last case corresponding to that of the blue sky, and the transmitted yellow light corresponding to that of the setting sun. The theory that the colour of the blue sky is due to the absorptive effect of ozone does not account for this polarisation (p. 586). It is of interest to note that the light from the night sky shows very little polarisation (compare Rayleigh, *Nature*, March 17, 1921) For Lord Rayleigh's recent work on the light scattered by gases in respect of polarisation, see the references given in the CHEMICAL NEWS, 1921, cxxii, 34; and also *Nature*, 1917-1918, and *Comptes Rendus*, 1920, clxxi., p. 1002, with reference to the work of Cabannes on the "Light Diffused by Argon").

*Note.*—The work by Dr. H. S. Hele-Shaw and others on the production of coloured bands by water in a state of tension may have some connection with the colour of water, but the subject is too complex to be entered into here (see *Nature*, 1898, lviii., 34, 520, 535; Osborne Reynolds, *ibid*, 467; Hele-Shaw, *ibid*, 1890, lix; *Rep. Brit. Assoc.* 1898; and for later developments, C. J. Coker, *Engineering*, 1921, cxi., 1; and also March 24 and 31, 1921).

*The Molecular Formula of Water.*

The molecular formula of water at 0° corresponds to $(H_2O)_4$, according to the surface tension method of Eotvos (Ramsay and Shields, *Zeitschr. physikal Chem.*, 1893, xii., 433; *Phil. Trans.*, 1893, A, 662; *Zeitschr. physikal Chem.*, 1893, xii, 464; and the "Molecular Complexity of Liquids," *Journ. Chem. Soc.*, 1893, lxiii., 1089). This is a high value for a liquid, and water has also a large dielectric constant, 77 at 18°, in which, however, it is exceeded by liquid hydrocyanic acid (*Zeitschr. physikal Chem.*, 1902, xxxix., 217), $H_2O_2$, and formamide (Walden, *Trans. Far. Soc.*, 1910)

The dissociation of water increases with rise in temperature (Noyes, Carnegie Institution of Washington, Monograph No. 63) and this is explained (by Holmes) because water at low temperatures contains only a few molecules of $H_2O$, most of the molecules being polymerised; with rising temperatures these molecular complexes break down into simple molecules $H_2O$, of which the number in water is rapidly increasing with rising temperature. It is quite possible that whilst the percentage of $H_2O$ molecules actually dissociated into ions, like other substances, decreases with rise in temperature, the concentration of the ions in pure water would increase until a large part of the polymerised water molecules had broken down into the simpler molecules, which only occurs at a comparatively high temperature.

Ramsay and Shields (*loc. cit.*) found the value of the association for water at its boiling point to be 2.66; whilst P. A. Guye (on the "Nature of Molecular Associations in the Special Case of Water," *Trans. Far Soc.*, 1910, vi., 84) found the value 1.96, which, however, agrees with other determinations. Bousfield (*ibid*) pointed out that if this value were accepted, Sutherland's theory that liquid water is a mixture of di- and tri-hydrols becomes untenable, because if water is associated above 100°, monohydrol must exist in considerable amounts to lower the average association value to less than 2. I do not see how this follows—the monohydrol might quite conceivably be produced by decomposition of di-and tri-hydrols with rising temperature (0° → 100°+); but, in any case, Guye's values are uncorrected for equation of state (see Kendall, CHEMICAL NEWS, 1921, cxxii., 32).

T. M. Lowry and W. A. Bousfield (*Trans. Far. Soc.*, 1910, vi.) have proved that it is absolutely necessary to assume the existence of mono-, di-, and trihydrols in order to account for these complex changes and those occurring with solutions in water.

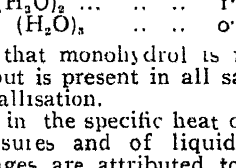
Sutherland (*Trans. Far. Soc.*, 1910, vi.) suggested that the hexagonal symmetry of ice crystals as evidence in favour of the trihydrol formula (for ice). He calculates the following densities :—

| | | Density. Solid. | Liquid. |
|---|---|---|---|
| Monohydrol, $H_2O$ | .. ... | 1·37 | 1·26 |
| Dihydrol $(H_2O)_2$ ... | .. .. | 1·13 | 1·09 |
| Trihydrol, $(H_2O)_3$ | .. .. | 0·92 | 0·88 |

and considers that monohydrol is not present in liquid water, but is present in all salts containing water of crystallisation.

The minima in the specific heat of steam under moderate pressures and of liquid water under moderate changes are attributed to the dissociation of complexes, which explanation also applies to the anomalous behaviour of water at 4°, its magnetic behaviour (*Comptes Rendus*, 1912), and the variation in viscosity and compressibility of water with temperature changes.

F. P. Sexton (*Trans. Far. Soc.*, 1910, vi.) calculated the specific heat of the first four molecules of water in $CuSO_4.5H_2O$ to be 0·499, and the fifth, 0·508 Senter (*ibid*) stated that, in compounds like $CuSO_4$.5aq. four molecules of water are probably definitely associated with the metallic atom, and the remainder perhaps attached to the molecule as a whole. This should be considered in connection with Mr. H. T. F. Rhodes' paper (CHEMICAL NEWS, 1921, cxxii., 85, 97), in which (p. 87), formula (A), accords with Senter. He also refers to Kohlrauch's ring formula for water (p. 86), which is probably in agreement with Sutherland's suggestion. According to this, sodium hydroxide should have the constitution




*i.e.*, $(NaOH)_6$

This would probably be determinable by surface tension measurements of liquid caustic soda. (See also Jackson, CHEMICAL NEWS, 1920, cxx., 80, for colour of $CuSO_4.H_2O$ and $CuSO_4.5H_2O$).

Mr. W. R. Fielding has now modified his theory of polymerisation in the solid state to conform with the view that ice at its melting point is $(H_2O)_3$, whereas he previously concluded it to be $(H_2O)_2$. Ramsay and Shields, however, determined it to be $(H_2O)_4$, whilst by X-ray analysis, it has recently been evaluated as $(H_2O)_2$ (D. M. Dennison, CHEMICAL NEWS, 1921, cxxii., 55). This latter value is a direct determination, and should, I think, be accepted.

From a consideration of the connection between association and dissociation, it has been concluded that non-associated liquids do not ionise substances dissolved in them, associated liquids do.

In conclusion, we may note the following investigations in this field: Armstrong, B.A. Rep., 1885, 962; Armstrong and Watson, *Proc. Roy Soc.*, 1907, A, lxxix., 579; Caldwell, *ibid*, 1906, A, lxxvi., 272; Whymper, *ibid*, 1907, A, lxxix., 576; lxxvi., 272; Whymper, *ibid.*, A, lxxxvii., 664; D. Berthelot, *Comptes Rendus*, 1900; and Porter, *Trans. Far. Soc.*, 1910, vi.

Finally, the theories as to the colour of water and ice may be thus grouped: (1) That the blue colour of pure water and ice is due to selective absorption of rays of complimentary colour, perhaps due to the molecular aggregation (Duclaux and Wollmann; H. T. Barnes; and also W Spring); (2) that the colour is due to scattering of light by suspended particles (Aitken, Abegg, &c.); (3) that the colour is due to a sky-effect; (4) that, in the case of sea-water, it is due to dissolved organic matter (Buchanan).

I think that (1) and (4) adequately explain all the observed facts.

6, Kitchener St., Walney,
Barrow-in-Furness.
4th April, 1921.

## THE PRESENT POSITION OF CHEMISTRY AND CHEMISTS.*

By Prof. N. T. M. WILSMORE.

THE tremendous events through which we have passed since the last meeting of the Australasian Association for the Advancement of Science have brought about changes in our social and economic conditions of so far-reaching a nature, that little apology is needed for attempting briefly to take stock of the resultant effect on the position of chemistry and chemists.

Many of the changes caused by the war are still in progress, whilst others are too recent to be viewed in their right perspective, so that with regard to most of them it is hardly possible as yet to decide which are for the better and which for the worse. Nevertheless, I think we have some ground for concluding that, on the whole, the effect of the war on the position of chemistry and chemists has been favourable. In any case, it has provided an object lesson of the national importance of chemistry, which the man in the street cannot afford to neglect. But much remains to be done before chemistry is generally recognised, as it should be, not only as an indispensable branch of exact knowledge, but also as one of the learned professions, not inferior in status, for example, to law, medicine, or engineering.

Prior to the war the status of science and scientists in the estimation of the Government and people of Britain, and of Australia, compared most unfavourably with that accorded to them on the Continent of Europe or in the United States of America; and in spite of the drastic lessons of the war, it is still far from satisfactory. It has been well said that the work of men of science like James Watt or Dalton or Faraday has done more to shape our modern social and economic life than any statesman or so-called "social reformer"—dare one, in this free country, even with bated breath, add "or Labour leader"?—who ever lived. Yet there is too much reason to doubt whether so much as five per cent of the elected representatives of the people in Britain or Australia could give an intelligent answer, if they were asked who Dalton or Faraday were, or what they did.

As Mr. H. G. Wells in his "Outline History of the World" so forcibly and clearly points out, the present cultural ascendancy of the European peoples does not necessarily prove their racial superiority over the peoples of Asia. This ascendancy dates back only some four hundred years, and is due primarily to the command over the forces of Nature, achieved by a relatively small number of devoted men of science. There is good reason to believe that amongst the Asiatic peoples men not inferior in ability, may be found, who, given suitable environment, might produce similar results. Already the Asiatic peoples are beginning to realise this possibility; and when their awakening is complete, the ascendancy of the European peoples may disappear as quickly as it arose. The progress made by Japan alone in one generation shows that our comfortable belief in the fundamental superiority of the European may be a dangerous delusion, and that any weakening in the pursuit of scientific knowledge means risk of losing our present lead, possibly for ever.

However, in Australia we may congratulate ourselves that some progress is being made. The Institute of Science and Industry has at last been put upon an apparently permanent basis, and has been voted an income of £15,000 per annum. Carping critics may say that for the task of co-ordinating and organising the application of exact knowledge to the industries of Australia this sum, in view of the depreciated value of our currency, is ludicrously inadequate. But on the other hand, it amounts to nearly one-third as much as the involuntary contribution which our grateful country is making to increases in Commonwealth Parliamentary salaries, so obviously science has no reasonable ground to complain.

The unsatisfactory status in British communities of science in general is unfortunately shared by chemistry and chemists. This does not mean that British chemists have to admit inferiority to those of other countries. Far from it On the contrary, they may justly claim that in the quality, and in proportion to their numbers, in the quantity also, of their contributions to knowledge, especially those of a pioneering nature, they need not fear comparison with the chemists of any other nation. Yet up to, and even after the outbreak

* Presidential Address, delivered before Section B (Chemistry) of the Australasian Association for the advancement of Science at the Meeting held in Melbourne.

of war, their efforts to secure adequate recognition of their science from manufacturers, Government, and people, were met for the most part with contemptuous indifference. Since chemistry includes the study of changes in matter and of the accompanying transformations of energy, there is scarcely any branch of productive activity which does not require some knowledge of chemical phenomena, and in which, therefore, the progressive developments of modern chemistry can safely be ignored. This truth, which is stated at the beginning of most elementary text-books on chemistry, is so familiar to chemists as to be commonplace. Yet the oft-recurring failure of others to appreciate it, and to make effective use of the chemical knowledge and skill available, had as its inevitable consequence that many of the British manufacturing industries, especially the more particularly chemical industries, were falling behind in the race for world supremacy; with the further consequence that we nearly lost the war, and with it our existence as a Great Power, possibly even as an independent nation

Fortunately for us there were notable exceptions to the general rule. For example, in one of the most important branches of applied chemistry in Britain, namely the steel industry, intensive research and scientific control had been for years the general practice in many of the works, with the result that, when the crisis came, the industry was able to respond to the enormous and varied demands which were made upon it. Another instance of the value of chemical research and control is given by the history of Brunner, Mond & Co., who, in the words of Prof Donnan, revolutionised the British alkali industry by introducing the delicate equilibria and reactions of Solvay in place of the rough-and-tumble heroics of the older Le Blanc process. The same policy enabled this firm to give invaluable help to the British Government in connection with the manufacture of high explosives After many months of war, the British War Office decided to follow the German and Austrian lead, by adopting in place of picric acid or pure T.N.T. for the bursting charge of high explosive shells the much cheaper but equally effective mixture known as "amatol" consisting of 80 per cent by weight of ammonium nitrate with only 20 per cent of T.N.T. The manufacture of ammonium nitrate had, therefore, to be developed on a very large scale, but owing to the great amount of data and experience on the application of the Phase Rule to the phenomena of solubility and crystallisation in connection with solutions of mixed salts, which they had been accumulating for many years, the research staff of Brunner, Mond & Co. were able rapidly to work out on a technical scale three extremely neat and efficient methods for this manufacture, starting in the one case from synthetic calcium nitrate, and in the other two from Chili nitre.

As examples of the estimation in which chemists have been held by Government officials, the following incidents are worth recalling. Early in 1915, when the demand for a vastly increased output of munitions of all kinds was becoming urgent, the War Office found itself obliged to increase the staff of the Research Department at Woolwich, and accordingly advertised for a number of research chemists. The qualifications required were a B.Sc. degree in chemistry, together with the Associateship of the Institute of Chemistry and experience in analytical work; and to chemists possessing these qualifications was offered the munificent salary of £2 0s. 0d. per week. At the close of the same year the British House of Commons Recruiting Committee, in attempting to classify vocations according to utility for munition and other work at home, issued the statement that the classes of workers which could most readily be spared for service in the Army were "*navvies, tunnellers, and chemists*!" On which the late Sir William Ramsay commented in a letter to the Press that, although this estimate of the value of chemists was doubtless due to ignorance, the men responsible for it had thereby shown themselves unfit to be trusted with the destinies of the Empire. But in this connection Australian officialdom was not to be outdone, for about the same time the Victorian Department of Mines advertised for a chemist with a B.Sc. degree and a sound knowledge of chemical analysis, to take part in research work on the distillation of brown coal and similar important problems, at the princely salary of £72 per annum!

Official indifference to science in general, and chemistry in particular, has cost us dearly, both in blood and treasure We know, for instance, that early in 1915 Germany was running short, not only of propellant explosives, but also of the particular raw materials, cotton and glycerin, required for making them. Yet, in spite of the repeated warnings of Sir William Ramsay and other eminent chemists, our blockade was so negligently enforced, that for the first 15 months of the war the importation into enemy countries of cotton and of fats and oils was allowed to go on almost unchecked. As an example of the kind of ignorant obstruction which chemists had to face, it will suffice to mention that a well-known technical chemist of my acquaintance, in the course of an interview on this subject with a high official of the War Office, was met by the reply that, if we stopped the importation of cotton-wool into Germany, the Germans would simply make their explosives from *sheep's wool* instead, and that there was therefore nothing to justify the risk which we should run of offending the United States! However, at last things began to move, for a little later we find the present Lord Chancellor (then Sir F. E. Smith), stating in the course of an argument in a contraband case before the Prize Court, that it had "just been discovered that glycerin could be made from lard." Although he was thus unconsciously celebrating the centenary of Chevreul's great discovery, it is perhaps better that the members of our "governing classes" should acquire scientific knowledge a little late than not at all. Unfortunately, by the time sufficient understanding of the elementary chemistry of explosives had penetrated the minds of the powers that be to induce them to make the blockade really effective, the chance for seriously hindering the German manufacture of propellant explosives was lost. During the respite so generously allowed them by the British Government, the German chemists had been able to develop a process for making from wood pulp a cellulose sufficiently pure and uniform to give a satisfactory propellant, thus making the German manufacture of explosives as independent of the importation of cotton as it had already been made of that of nitrates.

The exceptionally unsatisfactory status of chemistry in the British Empire may be ascribed to various causes One of these, and one which still operates to our detriment, has been the British Pharmacy Act of 1867, which has been adopted in principle throughout the Empire. For the most part this Act was admirable, as it not only gave legal recognition to the ancient and honorable profession of pharmacy, but also provided the public with a much-needed safeguard against the unchecked sale and incompetent dispensing of drugs possessing poisonous properties. But unfortunately, it contained one provision which has led to a most serious misunderstanding in the mind of the British public concerning the proper meaning of the word "chemist", and the rightful status of the chemical profession, a misunderstanding which is not found in any other civilised country. This provision forbids anyone but a chemist as defined in the Act to describe himself as such unless he has been duly registered as a "*chemist and druggist*" or a "*pharmaceutical chemist.*" Thus, to quote the Historian of the Institute of Chemistry of Great Britain and Ireland, "the President of the Chemical Society of London cannot in strict law call himself by the name by which he is known throughout the civilised world without breaking the laws of his country." It is difficult to believe that such a provision could have been passed by any legislature which was not pitiably ignorant of modern science. I understand that it has been adopted in a peculiarly obnoxious form in the State of Victoria. This deplorable but legalised annexation of the generic name of "chemist" by the followers of a specialised branch of applied chemistry is an example of a form of legislation which is fortunately rare. In fact, the only case at all parallel which I can recall, was when, somewhere about 1880, the Parliament of New South Wales, at the instance of the late Sir Henry Parkes, sought to have the name of that colony changed to "Australia."

It is pleasing to note that in other respects the relations between pharmacists and non-pharmaceutical chemists have been generally friendly. In fact, the British Pharmaceutical Society gave valuable help to the Institute of Chemistry, when, in 1884 and 1885, the latter was applying for its Royal Charter of Incorporation. Also in the meantime, many pharmacists seem to be coming to the conclusion that the name "chemist" is of questionable advantage to them, now that the public has been forced to realise that there are other important species of chemists, who have nothing to do with the dispensing of drugs or the sale of poisons. The signs of the times are therefore looking favourable to some reciprocal arrangement between pharmacists and chemists, whereby the former might consent to renounce the terms "chemist and druggist" and "pharmaceutical chemist" in favour of "pharmacist" or "apothecary," provided that the latter assist them to secure a stiffening up of the Pharmacy Acts, so that the dispensing of any kind of medical prescription, whether containing a poison or not, by anyone but a properly qualified and registered pharmacist would be prohibited Such an arrangement could, however, be carried through only gradually and cautiously, or unjustifiable hardship to the present holders of the vested interest in the titles "chemist and druggist" and "pharmaceutical chemist" would be caused. For example, any sudden demand to alter shop signs and labels would entail very serious cost. But the very fact that any such change must be slow requires that this matter should be taken up vigorously by responsible bodies of chemists without delay. In this connection, it is worth noting that friendly negotiations with the above end in view have been going on for some time in England between the Institute of Chemistry and the Pharmaceutical Society, with some promise of success.

Much of the indifference to science shown by the average layman, must, I fear, be ascribed to his school training. Although science teaching of a sort is becoming general in our secondary, and even to some extent in our primary schools, it is too often so unintelligent and perfunctory that to many pupils it probably does more harm than good. In British secondary schools the practice is extending of employing for the teaching of science subjects teachers who have gained a university degree, preferably with honours, in those subjects. In Australian schools, however, with some notable exceptions, the salaries offered are too low to attract science teachers of first-rate ability and adequate training. In other words, the teaching of science is frequently left to the type of teacher who is content to keep one page ahead of the pupil, and who is therefore unfitted to present the subject to the latter as a living thing, of fundamental importance in his daily life. Under such conditions, school science degenerates into a mere cramming of text-books, which, in accordance with the good old school precedent, seem to have been selected chiefly for their exceeding dryness, and the inevitable result follows, that the mention of science calls up in the pupil's mind a positive repugnance, instead of the interest which should stimulate him to pursue the subject further for himself. Sir Robert Hadfield has recently ascribed his early interest in science largely to that fascinating work, Pepper's "Playbook of Science," and in a humbler capacity I must make the same confession. In this and the companion volume, the "Playbook of Metals," which were not, and perhaps never could have been, school textbooks, Pepper developed the art of conveying exact information and sound scientific principles, and at the same time calling up a spirit of scientific romance which is peculiarly attractive to the average boy. Sir Robert Hadfield states that not long ago he presented several hundred copies of a modernised edition of the "Playbook of Science" to the elementary schools of Sheffield, with satisfactory results. It would be well if a little of the spirit of that book could be infused into school science textbooks generally. But it may be doubted whether any spirit of romance could survive the deadening influence of the examination system.

Scientific men as a body have suffered in the past from too much reluctance to push their claims to recognition. I do not mean that we ought to rush into a campaign of self-assertion; but there should be a happy medium, if we could only find it. In the first place, the frequent practice by scientific men of doing valuable work gratuitously for governments and other public bodies, although it may be clear evidence of a moral superiority, is bad business, and should be discontinued. In the estimation of governments

and the public, the value of scientific, as of other work, is a function of the price which they have to pay for it. The function is too complex for complete analysis, but this much is clear, that as the price paid for scientific work approaches zero, the value set upon that work by those who benefit from it also becomes zero, or even negative. Further, no other class of professional man is expected to work gratuitously for public bodies, and when scientific men do so, they have only themselves to blame if their modesty is regarded as a confession of professional inferiority. If scientific men do not stand together to uphold their just claims to adequate reward for their labours, they may be quite certain that neither Government nor public is going to lose any sleep on their account. That the matter is urgent is shown by the fact that quite a number of prominent chemists, whom I had hoped to see at this meeting, have written to say that they cannot afford the journey. If the effect of the high cost of living and travelling on men with fixed salaries is going to convert the Australia States into watertight compartments, so far as men of science are concerned, the prospects of science in Australia are not encouraging.

On the technical and industrial side chemists have fared unfavourably in professional status as compared with engineers. The reasons for this are not far to seek. The products of the engineer's labour are usually of a permanent nature, and appeal to the eye as definite and concrete achievements. The business or financial man believes that he understands them, and to some extent appreciates the difficulties which have been overcome in their erection Naturally, therefore, he respects the man who created them. Also the engineer during his training has usually seen something of the handling of labour, and has acquired sufficient knowledge of business to enable him to meet the purely business man on more or less equal terms. On the other hand, our hard-headed business man is apt to regard the chemist as either of doubtful utility or a suspicious character. So far as he can see, the chemist seems to be spending his time in juggling with invisible molecules and atoms and electrons, which, as a business man has put it, "are so small and insignificant that they haven't got any size to 'em"; and it is difficult to convince him that these insignificant things make up in numbers for what they lack in size, and that he who can control them will rule the world. It must be admitted that the training of the chemist has been largely to blame. More often than not he has had no chance during his training to get any insight into the handling of labour or into business methods, or the working of technical plant, so that he starts his works experience with a heavy handicap as compared with the engineer. Hence we so often find the management of a manufacturing concern, even when the processes involved are largely of a chemical nature, in the hands of purely business men, or at the most of engineers. In such cases the chemists, if employed at all, are reduced to the position of mere testers, and are discouraged from acquiring too much knowledge of the business, let alone offering suggestions or criticisms. The idea of a chemical research department is scouted as a costly fad, and the so-called "practical man," who in reality is usually the worst kind of hap-hazard theorist, reigns supreme. It is not surprising that chemical manufactures under such conditions tend towards stagnation. In fact, a business involving chemical processes cannot be run indefinitely on such lines with safety; sooner or later it must succumb to the competition of more progressive rivals. Experience has shown the great advantage to be derived from allowing the chemists to acquire a working knowledge of every detail of the business, and even to share in the management. Above all, facilites for research are essential, if progress combined with economy is to be ensured. It hardly ever happens that the working out of new processes or of improvements in existing processes is achieved without making mistakes. And it should be obvious, even to the purely business or financial man, that it is cheaper to make these unavoidable mistakes on a small scale in a research laboratory than on a large scale in the works.

(To be continued.)

## NITROTARTARIC ACID.

By ARTHUR LACHMAN.

ALTHOUGH nitrotartaric acid is the raw material of the important dye tartrazine, it has not been the subject of much published work; it is, however, a very interesting substance. It was first prepared by Dessaignes (Dessaignes, *ibid.*, 1852, liv., 731), by dissolving tartaric acid in strong nitric acid, and adding sulphuric acid to the mixture. He found it a rather unstable compound, and described its decomposition products quite accurately, although he overlooked the most important one, viz., dioxy-tartaric acid. This reaction was discovered by Kekule (Kekule, *Ann.*, 1883, ccxxi., 245). Dihydroxy-tartaric acid behaves like a diketone, and it is a condensation product of this diketone with phenylhydrazine sulphonic acid which forms the dye tartrazine.

There would seem to be little doubt, from its method of preparation, that nitrotartaric acid is really what its name implies, viz., the nitric ester of tartaric acid; yet it is usually referred to with quotation marks around the "nitro," or as "the so-called nitrotartaric acid." Its actual relationship to tartaric acid could only be brought out by *reducing* agents, such as ammonium sulphide; other reagents gave either *dihydroxy*-tartaric acid, or its decomposition products. It was an open question, therefore, whether nitrotartaric acid is not really a derivative of dihydroxy-tartaric acid, and thus an oxidation product rather than an ester.

### *The Constitution of Nitrotartaric Acid.*

It is very difficult to dehydrate nitrotartaric acid completely; if the material is left exposed to air, it slowly takes up more moisture, loses nitrous acid, and changes over to the dihydroxy acid. If the slightly moist nitro acid is stored in a stoppered vessel, on the other hand, the brownish fumes, which appear at first, soon vanish; and after an interval of several weeks, the bottle contains *nitric* acid fumes, and a hard crust which proves to be chiefly tartaric acid.

The hydrolysis of nitrotartaric acid into its original components may be hastened considerably. One and ninety-three hundredths grm.,

moistened with one drop of water in a test-tube, showed nitric fumes after four days; after six days, tartaric acid was determined by the Goldenberg method, and 1·07 grm. found, 89 per cent of the amount calculated. The same quantity of nitro acid was moistened with 1 cc. of strong nitric acid, containing 0·3 grm. of water (just sufficient for complete hydrolysis) when 1·12 grm. of tartaric acid was found, 94 per cent of the theoretical yield. The reaction in this latter case completed itself overnight.

The extent of this acid hydrolysis is strongly influenced by the proportion of water present. Thus, when 2·00 grm. of nitro acid was allowed to stand with 7 grm. of water and 2 grm. of nitric acid, only 0·15 grm. of tartaric acid was found, a 12 per cent yield, and when still larger proportions of water are used, only traces of tartaric acid make their appearance.

Tartaric acid is also produced by the action of a few drops of strong hydrochloric acid or of moderately diluted sulphuric acid. There is little doubt, therefore, that nitrotartaric acid is a true nitric ester in the presence of high concentrations of mineral acids.

*Preparation and Properties of Nitrotartaric Acid.*

*Preparation.*—To prepare nitrotartaric acid, it not necessary to use fuming nitric acid, as Dessaignes did. To 70 cc. of nitric acid (sp. gr. 1·42) add 50 grm. of *powdered* tartaric acid, and stir well. Add concentrated sulphuric acid (sp. gr. 1·83) slowly, with stirring, until the tartaric acid is all dissolved; then add the balance of the sulphuric acid (200 to 250 cc. in all). Allow the mixture to cool slowly for several hours. Filter off the excess of sulphuric acid on a Büchner funnel; ordinary filter paper may be used if moderate suction is applied. Stir the cake with about 300 grm. of ice until all lumps are broken up, and extract the mixture with ether. Wash the ether twice with small amounts of ice-water, and dry with calcium chloride for a short time. Evaporate the ether carefully on the water-bath until brown fumes begin to appear, then allow to evaporate spontaneously. The product, except for traces of water and dihydroxy-tartaric acid, is practically pure nitrotartaric acid. The yield is from 60 to 75 per cent.

*Properties.*—Nitrotartaric acid crystallises in soft, white needles, which interlace much like those of asbestos. It is quite soluble in water, very soluble in alcohol, amyl alcohol, acetone, ether; insoluble in ligroin, benzene, &c. If carefully dehydrated over lime or caustic soda, it seems to keep indefinitely in a perfectly dry atmosphere. As ordinarily obtained, it smells of nitrous acid; the perfectly dry acid is odourless. For analysis, the acid was dissolved in dry ether, and precipitated by benzene.

Alkalies act violently on nitrotartaric acid, even in very dilute or in alcoholic solution, with practically complete decomposition, as discussed below. It is, however, unexpectedly stable towards sodium carbonate, and on titration shows itself to be a dibasic acid.

Subs., 0·2949 : 0·1 *N* sodium carbonate sol., 24·8 cc. (Equivalent to 100·6 per cent nitrotartaric acid).

Working at 0°, a perfectly sharp end-point is obtained with methyl orange as indicator.

The strength of nitrotartaric acid is manifested by its action on calcium chloride when the latter is used to dry its ethereal solution. After several hours, the calcium chloride lumps are covered with a feathery mass, which after two days fills the entire liquid; the ether then contains nitrosyl chloride. The solid consists of a mixture of the calcium salts of nitrotartaric and dihydroxytartaric acids.

On careful evaporation of a concentrated solution of nitrotartaric acid in sodium carbonate, a solid sodium salt can be obtained, though in impure form. This salt, although extremely soluble, is not deliquescent. It seems to show an abnormal behaviour, which is still under investigation.

Moist nitrotartaric acid decomposes with some violence well below 100°; the perfectly dry substance, however, was heated in xylene to the boiling point of the latter, without change.

When solutions of nitrotartaric acid in water are allowed to stand, they soon turn blue, gases are given off, and much heat is evolved. If the temperature is kept under control by water cooling, the process lasts from one to two days. The gases consist at first of nitrogen trioxide; later they become colourless, and are composed of nitric oxide and carbon dioxide. The solution contains chiefly dihydroxy-tartaric acid, which may be precipitated by addition of sodium acetate, or carbonate as the very insoluble sodium dihydroxy-tartrate; it also contains tartronic and oxalic acids. The yield of sodium dihydroxy-tartrate is from 75 to 80 per cent.

Little or no *tartaric* acid is formed; the highest amount found in many different hydrolyses was 1·3 per cent of the possible yield; in a few cases its presence could not be shown by the Goldenberg method.

The formation of tartronic acid during the above-described hydrolysis is due to the decomposition of dihydroxy-tartaric acid, as shown previously by Kekule and by Gruber; the latter acid loses carbon dioxide and passes over into tartronic acid. The mechanism of this reaction is not clear, and it is now being investigated. The production of oxalic acid is due to a side reaction, viz., the oxidation of tartronic acid by nitrous acid,

$$C_3H_4O_5+4HNO_2=C_2H_2O_4+CO_2+3H_2O+4NO.$$

This was proved by slowly adding a solution of tartronic acid to sodium nitrite; a copious precipitate of sodium oxalate was obtained. Tartaric and dihydroxy-tartaric acids, treated similarly, gave no oxalic acid whatever.

*The Action of Alkalies on Nitrotartaric Acid.*

When nitrotartaric acid is neutralised with caustic soda, the action is accompanied by the immediate evolution of considerable heat. Regardless of dilution within ordinary limits, cooling to —5°, or use of alcohol as a solvent, the same results are obtained, viz., production of sodium nitrite in practically quantitative yield, and complete decomposition of the dihydroxy-tartaric acid. It is not necessary to give the experimental details of the numerous experiments that were made. Entirely similar results were noted when calcium hydroxide was employed. In place of dihydroxytartaric acid are found tartronic acid, as already noted by Skinner (Skinner, *J. Chem. Soc.*, 1898,

lxxiii., 488), and a considerable amount of oxalic acid. The latter probably owes its formation to intramolecular condensation of diketosuccinic acid, with simultaneous formation of glyoxalic acid.

$$COOH—CO—CO—COOH + H_2O = COOH—COOH + CHO—COOH.$$

This reaction is now being studied.

The identification and separation of mixtures of the various acids encountered is a difficult and tedious matter; tartronic and oxalic acids are particularly hard to separate quantitatively.

*Discussion of Experimental Results.*

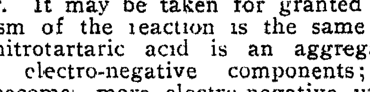
It has been shown that in the solid form, in the presence of strong acids, nitrotartaric acid is a true *nitrate* of tartaric acid. In aqueous solution, however, and when acted upon by alkalies, it behaves like a nitrite of dihydroxy-tartaric acid. The yield of dihydroxy-tartaric acid in the aqueous hydrolysis is good, considering the ease with which that acid is decomposed; and the yield of nitrous acid on hydrolysing with alkalies is almost quantitative. Nef (Nef, *Ann.*, 1899, cccix., 175), a number of years ago, showed that nitric esters of both fatty and aromatic alcohols yield considerable amounts of nitrous acid when saponified with alcoholic alkalies; the experimental conditions involved rather high concentrations of alkali, and the practical absence of water. In the present instance, the same reaction occurs in the complete absence of alkali, and in the presence of water. It may be taken for granted that the mechanism of the reaction is the same in both cases; nitrotartaric acid is an aggregation of strongly electro-negative components; benzyl nitrate becomes more electro-negative under the influence of alkalil.

The best explanation of the behaviour of nitrotartaric acid is that it passes over into a pseudo form as follows:

$$COOH—CH(ONO_2)—CH(ONO_2)—COOH \rightarrow COOH—C(OH)(ONO)—C(OH)(ONO)—COOH$$

This would appear to be a new type of tautomerism, involving the shifting of an oxygen atom instead of a hydrogen atom. The possibility of an hydroxyl group attached to nitrogen is excluded by the fact that nitrotartaric acid is only *di*basic; such a combination would almost certainly be strongly acid.

The suggested explanation of the formation of nitrous acid and a ketone in the case of nitrotartaric acid seems less forced than Nef's assumption of a "methylene dissociation" in the formation of nitrous acid and benzaldehyde from benzyl nitrate. It is much simpler to believe that benzyl nitrate isomerises to benzaldehyde nitrite,



which then loses NO—OH.

Nitroglycerin, like nitrotartaric acid, contains an accumulation of negative groups, and is therefore also sensitive to traces of acids, yielding nitrous acid and more or less complex aldehydes as first products, with rapidly increasing evolution of energy.

Owing to the comparative stability of dihydroxy-tartaric acid, it is possible to isolate it as the first product in the progressive decomposition of a nitric ester, and thus gain a clearer insight into the nature of explosive processes in general.

*Summary.*

1. Nitrotartaric acid is shown to be a true nitric ester of tartaric acid.

2. The decomposition of nitrotartaric acid in aqueous and in alkaline solution has been studied. The acid behaves as if it were the nitrous ester of dihydroxy-tartaric acid.

3. Nitrotartaric acid probably exists in two tautomeric forms, characterised by the shifting of an oxygen atom.

4. The decomposition of other nitric esters, such as nitroglycerin, is analogous to the behaviour of nitrotartaric acid.—*Journal of the American Chemical Society,* March, 1921.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

*Ordinary Meeting, April 14, 1921.*

Prof. C. S. Sherrington, President, in the Chair.

The following papers were read:—

"*Influence of Low Temperatures on the Magnetic Properties of Alloys of Iron with Nickel and Manganese.*" By Prof. K. Onnes, For. Mem. R.S., Sir R. Hadfield, F.R.S., and Dr. H. R. Woltjer.

1. A series of iron-manganese and iron-nickel alloys with a range of percentages of manganese and nickel respectively has been tested in order to investigate the influence of cooling to very low temperatures (liquid hydrogen and liquid helium) on their magnetic properties, especially to ascertain whether the iron-manganese alloys which are non-magnetic at atmospheric temperature become magnetic by so doing.

2. With a view to the desirability not only after, but also during immersion in liquid hydrogen, an apparatus has been constructed, which makes it possible to test the samples quickly one after another at a temperature of 20° K., with as little loss of hydrogen as possible.

3. The iron-manganese alloys, containing the higher percentages of manganese, cannot be made magnetic at atmospheric temperature by cooling to the boiling point of liquid hydrogen or liquid helium.

4. The existence of one magnetic and one non-magnetic, or at most slightly magnetic, manganese-iron compound is shown to be probable, and the non-magnetic properties of the higher manganese-iron alloys may be explained by their means.

"*Influence of Physical Conditions on the Velocity of Decomposition of Certain Crystalline Solids.*" By C. N. Hinshelwood and E. J. Bowen.

Experiments have been performed on the velocity of decomposition by heat of certain crystalline solids, such as potassium permanganate and ammonium bichromate. While in the case of liquid and gaseous systems the temperature coefficient of the reaction velocity allows calculation of a

"heat of activation" or "critical increment" of the reacting molecule, according to the method of Trautz, Lewis, and others, this calculation is not possible in the case of solids for various physical reasons connected with the propagation of the reaction from the surface into the interior. These are discussed in detail. On the other hand, the lowering of the velocity of decomposition of potassium permanganate when brought into solid solution in potassium perchlorate, indicates that the heat of activation of the permanganate is increased by the physical process of solid mixture. By equating this assumed increase in the heat of activation to the observed heat of solid mixture (obtained from the calorimetric measurements of Sommerfeld), approximate quantitative agreement is found between the observed rates of decomposition of potassium permanganate in various solid solutions and those calculated.

"*Adsorption of Gas by Charcoal, Silica, and other Substances.*" By Prof. H. Briggs.

The method of determining the adsorptive capacity of a substance at liquid temperature is described, and results are given of the capacity and manner of preparation or occurrence of 36 substances.

Charcoal and silica are compared, especially as relates to nitrogen and hydrogen, to illustrate preferential adsorption, and the influence of chemical composition on gas adsorption is discussed.

The effect of the compressibility of the initial layer, when the density of an adsorbent is determined by the immersion method, is considered An evaluation is made of (*a*) the volume of solid matter, (*b*) that of the interstitial space between the granules, and (*c*) that of the internal gaseous space for silica and cocoanut charcoal.

The density of the nitrogen adsorbed at —190° C. by silica and charcoal is calculated from experimental data. From these results it becomes possible roughly to estimate the error affecting the density of charcoal ascertained from water-immersion, and it is concluded that that method gave a result, for the writer's cocoanut charcoal, which was at least 0·55 too high. The conditions affecting adsorption at low and high saturation are set forth.

The presence of capillaries is not sufficient to account for adsorption. A high-capacity silica may be deactivated, and in the inactive state it remains porous. Graphite, which has no pores, adsorbs gas at —190° C. The evidence leads to the conclusion that deactivated silica is vitreous. It is argued that a vitreous solid, like a crystal, is a polymer, *i.e.*, a complete atomic linkage. The importance of distinguishing between the coarser capillaries or canals and the finer interpolymeral openings of an adsorbent is emphasised.

Activation is considered to be the effect of disrupting the solid polymers, and the means of accomplishing the partial depolymerisation of charcoal and silica is described.

"*The Properties and Molecular Structure of Thin Films of Palmitic Acid on Water.*"—Part I. By N. K. Adam.

The behaviour of films of palmitic acid on water has been investigated in detail to test Langmuir's views (1917). These have been confirmed and extended.

Films on water exhibit a resistance to lateral compression which is not shown by a clean surface of water. Resistance commences at $22 \times 10^{-16}$ sq. cm. per molecule (for palmitic acid), and increases linearly with further reduction of area until the force is sufficient to buckle the film. Collapse then sets in, and no further increase of force is regularly found necessary to diminish the area to zero. A metastable condition of increased resistance to collapse may however occur.

The compression curves point to the resistance being due to repulsion between the insoluble molecules, arranged in a single layer on the surface, each molecule being attracted to the water by its carboxyl group. The view that films two molecules thick exist appears to be quite irreconcilable with the curves observed. When collapse of the unimolecular film occurs, the molecules ejected are seen to aggregate into fine lines many molecules in thickness

The observed areas agree with the dimensions calculated from molecular volume studies, and the compressibility of the films is of the same order as for liquids in bulk.

The effect of acidity of the water on the films may be accounted for by the greater attraction of alkaline solutions than acid carboxyl groups. The observations indicate that the molecules are immersed further in alkaline than in acid solutions, even when alkalinity is insufficient to cause complete solution.

In still more alkaline solutions immersion becomes complete, and the molecules probably pass from the film into aggregates, having the hydrocarbon chains in the centre and the carboxyl groups on the surface. This structure is suggested for the "ionic micelle" of soap solutions.

"*On the Absorption of Light by Electrically Luminescent Mercury Vapour.*" By E. P. Metcalfe and B. Venkatesachar.

1. Experiments are described in which mercury vapour at low pressures, rendered luminous by the passage of small electric currents, is found to exert powerful selective absorption.

2. A list of wave-lengths found to be absorbed is given.

3. Photometric observations are recorded on the absorption and emission of 5461 A.U. by columns of mercury vapour of different lengths and carrying different currents.

4. The relation between the ratio (emission/absorption) and the current density is found to be linear.

5. The lines 5461 A.U. and 4359 A.U. have been reversed so as to appear dark lines on the white-light spectrum of a carbon arc and of the sun.

6. The reversal of 5461 A.U. has been studied in detail with a Fabry and Perot étalon and with an échelon spectroscope.

## NOTICES OF BOOKS.

"Physical and Chemical Constants and Some Mathematical Functions." By G. W. C. Kaye and T. H. Laby. Fourth Edition. London: Longmans, Green, & Co., Paternoster Row. Price 14s. net.

We are glad to find that in spite of the difficulties of production and of the numerous duties of

national importance that have fallen to the lot of at least one of the authors, it has been possible to revise and issue a fourth edition of this valuable work. The matter has been brought up to date. The chemical data has been recalculated on the basis of the International system of atomic weights. Among the additions to the book are tables of atomic numbers, X-ray wave-lengths, and terrestrial magnetic constants. The tables will naturally find a place in every laboratory. The size of the book is only slightly in excess of the last edition, and the design and binding is the same.

## BOOKS RECEIVED.

"The Combined Chemical Dictionary." Compiled and Edited by the Editorial Staff of the Chemical Engineering Catalogue. First Edition, 1919. 487 Pages and Index. The Chemical Catalog Co., 1, Madison Avenue, New York.

"Ammonia and the Nitrides, with Special Reference to Their Synthesis." By EDWARD MAXTED, Ph.D., B.Sc., F.C.S. With 16 Illustrations. Iv.+116 Pages. London: J. & A. Churchill. Price 7s. 6d. net.

"Critical Microscopy: How to get the best out of the Microscope." By ALFRED C. COLES, M.D., D.Sc. With 18 Illustrations. iv.+104 Pages. London: J. & A. Churchill. Price 7s. 6d. net.

"Inorganic Chemistry." By E. I. LEWIS, M.A., D.Sc. With Introductory Note by Sir Richard Threlfall, K.C.B. xv.+432 Pages. Cambridge University Press. Price 9s. net.

"The Extra Pharmacopœia of Martindale and Westcott." Revised by W. HARRISON MARTINDALE, Ph.D., F.C.S. and W. WYNN WESTCOTT, D.P.H. 17th Edition. Volume II. xx.+688 Pages. London: H. K. Lewis & Co., Ltd. Price 17s. 6d. net.

"Recent Practice in the Use of Self-Contained Breathing Apparatus." By Lieut. REX C. SMART, M.C., R.E. xiii +243 Pages. London: Charles Griffin & Co. Price 15s. net.

"Anthracene and Anthraquinone." By E. DE BARRY BARNETT, B.Sc., F.I.C. xi.+435 Pages. London: Bailliere, Tindall, & Cox. Price 27s. 6d. net.

## PAPERS RECEIVED.

"The Behaviour of Substances near the Absolute Zero." By WILLIAM RD. FIELDING, M.A., M.Sc., Vict.

From the specific heats of lead, copper, &c., at very low temperatures the author has calculated their degrees of polymerisation at the absolute zero. The minimum values he obtains are: $Pb_7$, $(H_2O)_{30}$, and $Cu_{150}$. The polymericular weights at the absolute zero are then plotted against absolute melting points, and by interpolation he obtains values for many other substances. $p$ (the degree of polymerisation) for the elements has a periodic value. Received April 18, 1921.

## NOTES.

PHYSICO-CHEMICAL PROBLEMS RELATING TO THE SOIL.—The Faraday Society is organising a General Discussion on the above subject to take place during the afternoon and evening of May 31 next. The meeting will be held in the Rooms of the Chemical Society, London, and it will be presided over by Sir A Daniel Hall, K.C.B., F.R.S., Chief Scientific Adviser to the Board of Agriculture. The Discussion will be opened by Dr. E. J. Russell, F.R.S., Director of the Rothamsted Experimental Station, who will give a general survey of the subject. A series of papers dealing with soil moisture, organic constituents, adsorption, and colloidal phenomena will then be put forward as a basis for discussion. It is expected that among those present will be Prof. Sven Oden, of the University of Upsala. Further particulars of the meeting may be obtained from the Secretary of the Faraday Society, 10, Essex Street, London, W.C.2.

ROYAL INSTITUTION.—At the Annual Meeting of the Members of the Royal Institution, held on the 2nd inst., Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair, the Report of the Visitors for the year 1920, testifying to the continued prosperity and efficient management of the Institution, was read. The number of new Members elected during the year was 54, a slight decrease on the previous year. 63 Day Lectures and 19 Evening Discourses were delivered, and the books and pamphlets presented to the Library amounted to 163, and the number purchased by the Managers 465, making a total of 628 volumes added to the Library during the year. Thanks were voted to the President, Treasurer, and Secretary, to the Committees of Managers and Visitors, and the Professors, for their valuable services during the past year. The following were unanimously elected as Officers for the ensuing year: *President*—The Duke of Northumberland; *Treasurer*: Sir James Crichton-Browne; *Secretary*—Colonel E. H. Grove-Hills; *Managers*—The Rt. Hon. Lord Blyth, Horace T. Brown, J. H. Balfour Browne, John M. Bruce, Sir James J. Dobbie, Percy F. Frankland, Alexander H. Goschen, The Rt. Hon. Earl Iveagh, H. R. Kempe, Sir Ernest Moon, Alfred W. Porter, Sir James Reid, Bart., Sir David Salomons, Bart., Sir Alfred Yarrow, Bart., The Rt. Hon. Sir Robert Younger. *Visitors*—James H. Batty, Alfred Carpmael, Frank Clowes, Edward Dent, Lieut.-Col. Henry E. Gaulter, George H. Griffin, W. E. Lawson Johnston, John R. Leeson, F. K. McLean, Edward M. Nicholls, Hugh M. Ross, Joseph Shaw, Sidney Skinner, Thomas H. Sowerby, William Stone.

THE Official Handbook of the British Association of Trade and Technical Journals has just been issued. The publications represented in the Membership of the Association number some 200, and embrace practically every class of industry. We note that engineering mechanics and electrical engineering exceed in number the publications of most of the other professions. The Handbook is convenient in size, and will certainly be useful, as it gives all the information as to date of issue, size price, advertisement rates, and particulars of all

the journals mentioned. The price of the Handbook is 1s., and the offices, Sicilian House, Southampton Row, London, W.C.1.

THE Printing Trades' Exhibition at the Royal Agricultural Hall will continue open until May 14. The Exhibition is very complete, one feature being a two day's Discussion, at which a long list of subjects is arranged. We note with pleasure no "ex-enemy goods" are permitted. Tickets can be obtained at the offices, 30, Fleet Street, E.C.

## New Patents.

THIS List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W.C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

10792—Mirat, G.—Manufacture of sulphuric acid. April 13th.
11039—Peace, E. L.—Manufacture of compounds of ammonia, etc. April 15th.
10615—Plauson, H.—Manufacture and treatment of viscose. April 13th.
10771—Pistor, J.—Manufacture of stable compounds containing oxygen and calcium. April 13th.
10792—Piperaut, P.—Manufacture of sulphuric acid. April 13th.

*Specifications published this Week.*

161244—Douglas, R. P.—Method of means for use in the manufacture of ammonia.
161253—Paris, A. J.—Process of cleaning and refining petroleum and analogous distillates.
161273—Kelly, A.—Manufacture of acid sodium pyrophostes.
161310—Wildman H. G.—Process for the extraction of alumina and its salts from clay.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

## MEETINGS FOR THE WEEK.

*Monday, May 9.*

Royal Institution, 5. (General Meeting).
Faraday Society, 8. "The Problem of the Fuel Cell" by E. K. Rideal and U. R. Evans. "The Solubility of Small Particles and the Stability of Colloids" by L. F Knapp. "Note on a Formula Expressing the Variation of Surface Tension with Temperature" by Prof. F. G. Donnan. Studies in Capillarity—Continuation of Discussion held at Manchester on the following papers: Part I—"Some General Considerations and a Discussion of the Methods of Measuring Interfacial Tensions" by Allan Ferguson. Part II—"A Modification of the Capillary Tube Method for the Measurement of Surface Tensions" by Allan Ferguson and P. E. Dowson.

*Tuesday, May 10.*

Royal Institution, 3. "Darwin's Theory of Man's Origin" by Prof. A. Keith.
Institution of Petroleum Technologists, 5.30.

*Wednesday, May 11.*

Royal Society of Arts, 4.30.

*Thursday, May 12.*

Royal Society, 4.30. "The Problem of Finite Focal Depth revealed by Seismometers" by G W Walker. "A Liquid Oxygen Vapourizer" by E. A. Griffiths. "Some Experiments on the Catalytic Reduction of Ethylene to Ethane" by Dorothy M. Palmer and W. G. Palmer. "The Catalytic Activity of Copper" by W. G. Palmer. "The total Heat of Liquid Carbonic Acid" by Prof. J. F. Jenkin and D. N. Shorthose. "Viscosity and Molecular Dimensions of Gaseous Cyanogen" by A. O. Rankine.
Royal Institution, 3. "Psychological Studies—The Appreciation of Music" by Dr. C. S. Myers.
Institute of Chemistry. (At Liverpool).

*Friday, May 13.*

Royal Institution, 9. "The Determination of Sex" by Dr. W. Bateson.
Physical Society, 5.

*Saturday, May 14.*

Royal Institution, 3. "Chemical Reaction" by Dr. E. C. C. Baly.


## NOTICES.

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## SOCIETY OF GLASS TECHNOLOGY.

THE Fourth Annual General Meeting of the Society of Glass Technology was held in the Chemistry Lecture Theatre, University College, Gower Street, London, on Wednesday, April 20, 1921, at 2.30 p.m.

The Secretary, Prof. W. E. S. TURNER, read a letter he had received from the late Lord Moulton's secretary. Lord Moulton, it was stated, "was looking forward to the dinner of your Society, but we can only regret that we all missed the inspiration which he would have given to your work in the future. He died, as he would wish to have died, in harness, but *we* can't help realising how necessary he was just now by reason of his great appreciation of England's scientific needs."

A number of amendments of the "Constitution and Rules" were approved, mainly with the object of making possible the election of honorary members. The Fourth Annual Report for the year 1920 was adopted. This showed that the total members on the roll at the end of 1920 was 620, 128 members having been elected during that year. The income and expenditure account showed a small deficit in the year's working. This was due to the increasing expense incurred in printing the *Journal*.

The following were then elected as officers of the Society in place of those retiring in accordance with the Society's rules.—

*President*—Morris W. Travers, D.Sc., F.I.C., F.R.S. (in place of S. N. Jenkinson, M.B.E.).

*Vice-Presidents*—Major W. L. Foster, C.B.E., D.S.O.; W. J. Rees, F.I.C.; F. Sweeting.

*Members of Council*—T. E. Barron; G. Wilson Clarke; F. E. Lamplough, M.A.; F. Lax; C. C. Paterson, O.B.E., M.I.C.E., M.I.E.E.

*Treasurers*—F. G. Clark (General); W. M. Clark, Ph.B. (American).

*Secretary*—Prof. W. E. S. Turner, O.B.E., D.Sc., M.Sc., F.Inst.P

*Assistant Secretary*—C. J. Peddle, M.B.E., D.Sc., F.I.C.

*Auditors*—Dennis Wood, F.S.A.A.; F. P. Wainwright.

A hearty vote of thanks accorded to the retiring officers was replied to by Mr. S. N. Jenkinson.

The new President, Dr. MORRIS W. TRAVERS, F.R.S., then delivered his Presidential Address on *"The Importance of Quantitative Investigation in Dealing with Technical Problems in the Glass Industry."*

Before proceeding to the subject of his address he wished to pay tribute to the memory of two great men, whose names the place and occasion called to mind. He referred to Sir William Ramsay, under whom he was trained as a chemist, and upon whose staff in University College he had served for nine years. The discovery of argon, the starting point of Sir William Ramsay's greatest discoveries, was the outcome of accurate quantitative investigation. Lord Moulton, who was to have presided at the dinner that evening, when in charge of the Department of Explosive Supply, had insisted upon the observance of the principle that industrial processes must be based upon quantitative ivestigation, with the result that whenever his Deparment took over a factory it was almost invariably found possible to increase the efficiency of the processes carried out in it. His services to the country went far beyond the reorganisation of a great part of our chemical industry, and on the observance of the principles which he laid down depended, in a great measure, our success in the future.

Efficiency resulted from the economic use of money or credit, labour, materials, and energy, and was only possible when the losses under each heading could be accurately ascertained. The energy balance sheet was really as important as the financial balance sheet, and each should be drawn out with equal care. The position of the skilled accountant was clearly recognised, but, in most works, very little was known about the disposal of the energy, which was only dealt with in terms of tons of coal. It would be impossible to check waste of money if one merely kept account of gross receipts and expenditure. It was equally impossible to check waste of energy if one knew only the total fuel consumption in a furnace. Each furnace should be studied with a view to ascertaining whether unnecessary losses could be checked, the fuel consumption reduced, and the efficiency increased.

In a recent paper submitted to the Society the whole of the thermal and chemical changes taking place in a plant consisting of a steam-air blown gas producer, and a tank furnace melting soda lime bottle glass had been dealt with, and an attempt had been made to show how much of the total energy of the fuel could be utilised in melting the glass, upon what conditions the efficiency of the plant depended, and where losses occurred. The investigation had been carried out for his own information, and the results had surprised him, and also the members of the Society who were present when the paper was read. The work had also brought to light the fact that a great deal of fundamental work remained to be done before they could deal effectively with glass furnace problems. The investigation of the nature of gas-producer tar, its composition, heat of formation, and its influence on the efficiency of heat exchange in the furnace should be investigated. We also required certain information as to the actual temperatures of the gases as they entered and left furnaces. The thermochemistry of the melting and plaining of glass required further study.

Furnace design should be based upon quantitative knowledge of the laws which governed the flow of gases through channels and spaces. The outlet flues from a pot furnace were not made small in order *to keep the heat in the furnace*, but because the velocity of the gas through a flue of small section was necessarily high, and when the velocity of the outflow was high, comparatively large fluctuations in the pressure in the furnace induced relatively small changes in the rate of outflow. With small flues it was easier to maintain steady conditions than when the flues were large.

As an illustration of the value of quantitative investigation of furnace problems, he showed how it was possible to arrive at an estimate of the loss of heat through the crown of a tank furnace, and

of the relationship between the value of the heat saved per year and the cost of increasing the thickness of the crown of the furnace.

The study of the process of melting and plaining glass, and investigations bearing on the nature of the glass itself, offered a very wide field for research. Many facts suggested that glass in the *solid* condition resembled the elastic gels more closely than simple liquids. At a discussion at a meeting of the Faraday Society he had suggested that the discovery of Peters and Cragoe, of the American Bureau of Standards, of the abnormal expansion of glass in the neighbourhood of the softening temperature might lead to a parallel in the case of gels, the density of which was known to be considerably greater than the sum of the densities of their constituents. Experiments which he and Mr. Taffel had carried out confirmed this prediction, and they had embarked upon an investigation of the thermal properties of glass, hoping that the results might throw light on the nature of glass. He referred to other investigations bearing on this problem.

In conclusion, he dealt with functions of the scientific man and the practical man in industry, and the need for their co-operation in the solution of technical problems.

There followed a paper on "*Automatic Glass Feeding Devices*," by G. Dowse and E. Meigh, M.B.E., M.Sc. This paper was given by Mr. Meigh. It was illustrated by lantern slides and by a kinematograph film showing the Hartford-Fairmont feeder in operation with Lynch machines. It gave an informative survey of the development of the art of delivering molten glass automatically to forming machines. It dealt with the various patents chronologically in three main steps or periods: (a) up to 1900; (b) 1900-1914; (c) from 1914 onwards. It was stated that during the last period of development there had been a perfect deluge of patents granted for feeders. This sudden rush of invention was due to several causes. The semi-automatic machines had come into use in America, and the increasing shortage of boy labour led to the elimination of the transfer boy and the development of the "no-boy" machine. The gatherer was now the only human element left between the furnace and the taker-in, and it was a logical step to replace him by mechanism. The most advanced method of automatic feeding was on the "gob" principle (the "gob" being an embryo bottle or jar nicely calculated to suit the dimensions of the parison mould). This method was being developed to-day for sound physical reasons, and experience had already shown that "gob" feeding possessed considerable advantages over the cruder flow feeds of various types. Special reference was made to the Hartford-Fairmont system. In conclusion, it urged for far more serious attention to automatic feeding devices by British glass manufacturers anxious to advance the country's interests. It pointed out that the adopting of automatic processes converted glass manufacture from a small-scale, many-unit, skilled craftsman's constant personal triumph over miserably poor and inefficient equipment into an engineering enterprise of the first magnitude. Unfortunately, in Great Britain glass engineering problems had been so neglected, and the dearth of glass engineers was so painfully severe, that the industry could not rise to its opportunities. During the war, and since, giant strides had been made in the application of science and scientific methods to the glass industry, and this had resulted in the industry being left with a large balance of information which it was totally unable to digest and utilise commercially, because it was deficient in the knowledge of the technique of glass manufacture and lacked adequate engineering personnel. Sheffield University had provided for the industry the chemists and the physicists. Let it now take the opportunity in both hands and provide the glass engineers, for unless trained glass engineers were forthcoming, the introduction of automatic glass-making machinery into our glassworks could be quite abortive.

The Third Annual Dinner of the Society was held on Wednesday evening, April 20, at the Hotel Cecil, London. The President, Dr. M. W. Travers, presided. The guests included A. Chaston Chapman, F.R.S., President of the Institute of Chemistry, Prof. F. J. Cheshire, Imperial College of Science and Technology, Dennis Herbert, M.P., Wm. Ide, Master of the Glass Sellers' Company, and R. S. Whipple, President of the Optical Society.

Following the toast of "The King," the toast of "The Society of Glass Technology" was proposed by Mr. A. Chaston Chapman. In the course of his reply Dr. Travers referred to the legislation recently proposed by the Government for the protection of the scientific branch of the industry. The view that the tariffs suggested were unsuitable and inadequate was held not only by the manufacturers, but also by the scientific and industrial worlds dependent upon supplies of chemical glassware. The only assistance which would enable this particular branch of the industry to continue was the total prohibition of all chemical glassware except under licence. It was a matter of great regret that electric lamp bulbs had not been provided for in the bill. The war had shown how extremely important these articles were, and it was felt strongly that the Government should be made to realise the importance of the question. Such assistance should be provided as was necessary to enable the manufacture of electric lamp bulbs to be continued in this country.

Mr. Dennis Herbert, M.P., submitted the toast of "The Glass Industry." It was one of the industries that saved the country during the war; but it was now suffering from the unfair competition to which it was now subjected owing to the depreciation of the exchanges in Germany and Austria. He trusted that the assistance proposed by the Government would be of some use in alleviating the hardship of competition without opposing the economic laws too directly. The production of chemical and scientific glassware was a key industry. It should therefore be protected by absolutely forbidding the entry into this country of former enemy goods which would tend to destroy the maintenance and progress of the industry.

On the following day a party of some 50 members of the Society travelled to Greenford to inspect the newly-erected works of Messrs. Rockware Glass Syndicate, Ltd. Here they were met by Mr. J. H. O. Bunge and Mr. Ed. Meigh. A most instructive time was spent, of special interest being the Hartford-Fairmont feeders operating in conjunction with Lynch machines.

# ATOMIC ENERGY AND RADIATION FROM THE SUN.

By F. H. LORING.

THE enormous output of radiant energy from the sun has been attributed to two causes, viz: (1) contraction of its mass, and (2) radioactive disintegration of its atoms. In the *Encyclopædia Britannica*, 1911, p. 88, a brief mention is made of these two causes of heat in the sun. It is stated that a source of heat which seems plausible "is rearrangement of the structure of the elements' atoms." So far as the present writer is aware, no connection between these two sources of energy has been suggested.

It is of course known that the heavier atoms of the Periodic Table exhibit radioactive properties; and in the case of the sun its mass is so great (see Table I.) that contraction would account for the emission of considerable radiant energy; but, in the latter case this energy has not been supposed to be sufficient to account for the enormous output of energy known to take place.

Looking at these matters from a general point of view, it would seem that in some way *pressure due to largeness of mass* might be a factor in both phenomena.

If one considers the atomic edifice to have a fixity of structure and a cohesive property which arises from the atomic electrons, positive and negative, so that the rigidity of matter and the definite atomic domains (Bragg) are due to the operation of electric and magnetic forces, as partly suggested by the Lewis-Langmuir atomic theory and the work and views of other physicists, then it becomes evident that these forces play a prominent part in giving to various atomic configurations or aggregations the observed physical properties of matter.

It is possible to show that these forces which give rise to both mechanically resistant and cohesive properties of matter are primarily due to what might be termed the kinetic state of the atomic constituents; in particular, to the negative electrons, which are presumably in rapid movement. Should the active systems resembling planetary systems be sufficiently disturbed, an outburst of energy from the atom might result; and, in the case of the radio-atoms, the energy of these systems appears as ejected particles, consisting of helium nuclei and negative electrons. If these ejected particles strike the atoms or molecules of a gas (in reality they probably pass more or less through them) ionisation results. M. N. Saha has studied the sun's spectrum from the point of view of ionisation potentials obtained in the laboratory. In the *Philosophical Magazine*, 1920, xl., pp. 472 and 809, Saha points out that the variations, as partly indicated by Table II., may be explained on the basis of a varying response of the elements to stimulation modified by the internal structure of the atom. All the known elements are supposed to be present in the sun, but they vary in response to ionising stimulation due to temperature. The enhanced lines are thought to be due to ionised atoms which are known to respond in a varying manner according to their ionisation potentials. Taking into account various ionisation potentials associated with different elements at different temperatures and pressures, calculations have been made which agree fairly well with the observed peculiarities. Referring to Table II., the data contained in columns (*e*) and (*f*) were not, of course, considered by Saha, as they are of very recent date.

Now in the case of the radio-atoms, largeness of mass appears to be associated with the phenomenon of radioactivity. It seems possible, therefore, that when the contraction due to mass is sufficiently great, the mechanisms of the atoms which give to them their "atomic domains" may cease to perform their normal functions; that is, cease in keeping the atomic constituents in their stable positions, and consequently, the systems may break up, and the energy of the component parts may appear as radiation. This is in general agreement with Bohr's theory, since in this case radiation is supposed to take place when the electron falls towards the nuclear part of the atom

Therefore, the cause of radiant energy emission from the sun may be due primarily to the *pressure within its more central mass*, and the atoms suffering such a pressure may break up, or disintegrate; the internal kinetic energy of the atom being liberated as in radio-active phenomena. In fact, one could imagine the sun to be, as it were, a vast radioactive atom whose mass is so great that the forces of its ultimate parts become disturbed; and a radioactive process, the same as that of a disintegrating atom of radium, for example, takes place, thus giving rise to an enormous output of radiant energy. The solar atmosphere, or envelope, may be bombarded from within by nuclear particles and electrons from disintegrating atoms, which action produces gaseous ionisation.

If this idea be true, then it should be possible to induce radioactivity by subjecting atoms to enormous pressure. To produce artificially sufficient general pressure to cause atoms to disintegrate may not be physically possible. Sir E. Rutherford's experiments (see CHEMICAL NEWS, 1921, cxxii., 169) however, seem to be in harmony with this idea; for Rutherford has succeeded in breaking up the nitrogen atom by bombarding it with high-speed -particles. In the case of aluminium, the bombardment gave rise to the liberation of H-atoms, which had an energy 25 per cent greater than that of the incident $\alpha$-particle. These experiments seem suggestive in this connection, for here is a case of an ordinary atom being artificially disintegrated by the blow or instantaneous pressure of the -particle ejected from radium C.

It might seem possible to trace a connection between the spectrum lines of the elements in the sun and the susceptibility of such elements to disintegration by the above method of Rutherford. The absence, for instance, of certain lines might be due to the elements having already been disintegrated by the radioactive change induced by the pressure leaving more of the less-breakable ones in evidence. This observation is supported by the absence of the spectrum of nitrogen, as this element is more easily broken up than some others. It is of possible interest to compare the data concerning certain elements in the sun and others apparently absent, as given by Saha (*loc. cit.*), with the behaviour of these elements bombarded with $\alpha$-particles (Rutherford, *loc. cit.*). From Table II. it will be seen that there is just

such an agreement as one should expect, save for two or three exceptions, but any element present in the sun in great abundance might, obviously, account for discrepancies of the kind in question. *Solar physics* and *the structure of the atom* are really closely allied subjects, and great advances may be anticipated in these departments in the near future.

TABLE I.

| | |
|---|---|
| Mass of the sun taking the earth as unity ... ... ... ... ... ... | 329,390 |
| Temperature of the sun's photosphere ... ... ... ... ... ... | 7500° Abs. |
| Temperature of the sun's chromosphere ... ... ... ... ... ... | 6000° Abs |
| Mean mass of the radio-atoms (H = 1·00) ... ... ... ... ... | 222 |
| Mean mass of the radio-atoms taking an electron as unity about ... | 404,000 |

TABLE II.

| Elements not found in the sun. (*a*) | Elements of doubtful existence in the sun. (*b*) | Elements giving faint lines in the Fraunhofer spectrum. (*c*) | Elements which appear not to have been investigated as regards their presence in the sun. (*d*) | Elements whose atoms give long-range H-atoms under bombardment with α-particles from RaC. (*e*) | Elements whose atoms do not appear to be disintegrated by the α-particle bombardment, or which do not give long-range H-atoms on bombardment. (*f*) |
|---|---|---|---|---|---|
| B | Ne | K | F | B | He |
| N | Ar | Cu | Cl | N | Li |
| P | Kr | Zn | Br | F | Be |
| S | Xe | Ge | I | Na | C |
| As | Ru | Ag | Te | Al | O |
| Se | Ta | Cd | &c. | P | Mg |
| Rb | W | Sn | | | Si |
| Sb | Os | Pb | Ionised atoms of the high-level chromosphere. | Other elements known to exist in the sun. | S |
| Cs | Ir | | | | Cl |
| Pr | Pt | | | | K |
| Tl | Ra | | | | Ca |
| Bi | Th | | (*g*) | (*h*) | Ti |
| | U | | Ca | He | Mn |
| | | | Sc | O | Fe |
| | | | Ti | Na | Cu |
| | | | Fe | Mg | Sn |
| | | | Sr | &c. | Au |
| | | | Ba | | |

*Summary.*

Saha's papers on ionisation in the sun afford some data as to the elements present therein, which together with (1) Rutherford's experiments in breaking up atoms by bombarding them with α-particles from RaC, and (2) the well-known fact that the radio-elements comprise atoms of greatest mass, and (3) the enormous mass of the sun, seem to suggest that the contraction of the sun's central mass forces atomic nuclei so close together that the constituents of atoms in rapid movement come into conflict, and an unstable state is impressed on them whereby radioactive disintegration takes place. Such a process should give rise to the bombardment of atoms in the envelope of the sun, and ionisation with radiation should ensue. Similarly, in the case of the radio-elements, their large mass may give rise to instability. A Table is prepared which shows that those elements from which Rutherford has obtained long-range H-atoms generally correspond to those elements not present in the sun; and, according to this hypothesis, they are the more disintegrable ones and they have in consequence been reduced in quantity by the above action, so that those remaining are the more resistant, except in one or two cases, which could be explained on the assumption that the elements in question are in greater abundance. Conversely, those elements the atoms of which seem to resist disintegration are more abundant in the sun. Solar physics and the structure of the atom are allied subjects, and great advances may be expected in these two important departments of science.

## NOTE ON THE PREPARATION OF CHLORACETYL CHLORIDE.

By E. DE BARRY BARNETT, B.Sc., F.I.C.

CHLORACETYL chloride can be prepared by the chlorination of acetyl chloride (Jazukowitsch, *Zeit. f. Chem.*, 1868, 234; Wurtz, *Annales de Chimie* (3), xlix., 60), but the product obtained by this means almost always contains higher chlorinated substances such as dichloracetyl chloride. It can also be obtained by treating chloracetic acid at 100° C. with phosphorus trichloride, but the reaction is a violent one, and it is extremely difficult to obtain a product which is free from phosphorus. For this reason, Frankland and Patterson (*Trans. Chem. Soc.*, lxxix., 190) preferred to prepare the substance by treating a mixture of chloracetic acid and phosphorus pentoxide with anhydrous hydrochloric acid gas at 200° C., a process which has obvious disadvantages for use in the laboratory.

It has been shown by Heumann and Köchlin (*Ber.*, xvi., 1627) that in many cases carboxylic acids are readily converted into their chlorides by the action of thionyl chloride, and it has now been found that the action of thionyl chloride on chloracetic acid affords a very convenient method for the preparation of chloracetyl chloride. In preparing acid chlorides by means of thionyl chloride, Heumann and Köchlin used excess of thionyl chloride, as owing to its low boiling point (78° C.) it was easy to remove excess by distillation. Chloracetyl chloride, however, has a comparatively low boiling-point, so that it is preferable to choose conditions such that the product still contains some unchanged chloracetic acid. Chloracetic acid boils at 190°, and there is no difficulty in separating it from chloracetyl chloride by distillation.

The following method was found to give excellent results. 95 grms. of chloracetic acid and 130 grms. of thionyl chloride were placed in a flask provided with a reflux condenser and heated gently on the water-bath for two hours. Hydrochloric acid and sulphur dioxide were evolved, and the heating was so regulated that the evolution of gas was never very rapid. The end of the condenser was attached to a calcium chloride tube so as to prevent the absorption of atmospheric moisture. At the end of two hours the evolution of gas was very slow, and the contents of the flask were then boiled briskly over the flame until

it completely ceased, which was usually found to be the case at the end of about half-an-hour. The resulting liquid was then distilled and the fraction boiling at 100-110° C. collected. This weighed 85-90 grms. The residue in the flask weighed 20-25 grms., and consisted chiefly of unchanged chloracetic acid which crystallised on cooling. It was used together with more chloracetic acid for the preparation of further quantities of chloracetyl chloride, and by doing this, the total yield of chloracetyl chloride was found to reach 95 per cent of that theoretically possible.

In the literature (Beilstein, "Handbuch der organ. Chemie," 4th Ed., vol. iii., p. 199) the boiling point of chloracetyl chloride is given as "about 105° C." This figure seems to be a little too low as 200 grms. of chloracetyl chloride prepared by the above method when distilled with a Young's 8-pear column passed over almost completely at 108-110° C. at 764 mm.

In the above preparation, technical chloracetic acid was used which was first purified by distillation and was found to boil constantly at 190° C. The crude product was yellow in colour, but the distilled acid was snow white. Technical thionyl chloride was also employed. It was purified by distillation with a Young's 12-pear column, and under these conditions passed over at 75-78° C.

## THE PRESENT POSITION OF CHEMISTRY AND CHEMISTS.*

By Prof. N. T. M. WILSMORE.

(Continued from p. 211).

It is often contended, however, that the expense of a research department can be dispensed with, on the ground that a purely business and non-technical management can always call in expert knowledge when it needs it; but this is apt to be a sort of fool's paradise. In the first place, the purely business management may not know when expert advice is needed. In the second place, as I once ventured to point out to a gathering of business men, the wise choice of experts itself requires a certain amount of expert knowledge. In the estimation of the average layman, the claims of the real expert are apt to compare unfavourably with those of the quack, because the expert, having a reputation to lose, is unable to promise so much. Hence the quack will probably get the job. Instances where something like this has happened in connection, for example, with State enterprises, will probably be familiar to most of us.

The claim is still too often made, and received with approval, either explicitly or by implication, that the man who is ignorant of scientific or technical matters is for that reason specially fitted to take what is called a "broad view" of them, and therefore to control them. The view he takes will be "broad" enough, but at the same time, it will be found to be shallow and inaccurate, and the control which he exercises is usually pernicious. It may be admitted that the ultimate aim of every manufacturing business is to make money, and that the crucial test of every process used in that business is whether or not it will pay. Nevertheless, the experience of the past generation has shown repeatedly and conclusively that when the control of a manufacturing business becomes vested solely in the hands of financial men, the prosperity of that business is in danger. The successful chemical manufactures have been those in which chemists and engineers have had a share in the management, whilst those in which the exclusive control has been captured by finance have for the most part gone to the wall. The outstanding example is, of course, the history of the manufacture of synthetic dyes in Germany and Britain respectively.

The chemist must, however, beware of appearing to claim that in industrial matters he can supersede the business man. The successful conduct of a manufacturing business demands an intimate knowledge of buying and selling, and of finance, which the chemist has seldom had the opportunity or aptitude to acquire. The combination in the same individual of high scientific and technical attainment with acute business and financial capacity, although occasionally met with, is too rare to be counted as a normal factor in every-day practice. On the other hand, the dividing line between chemists and engineers is becoming less strongly marked. That growing and already important class of experts, the engineer chemists or chemical engineers, having a working knowledge of both chemistry and engineering, have shown themselves eminently fitted for such tasks as the planning of works and for positions of control. But in the nature of things, it is not possible for any engineer chemist to have a complete mastery of both branches, so that in the working out of details, and especially for research, he will frequently require the help of both chemists and engineers. Hence for the sound development of a manufacturing business involving chemical processes, we must look to collaboration on more or less equal terms between the chemist, the engineer, and the business man. Each of these classes should be represented on the Board of Directors, or its equivalent.

With the outbreak of the war came the great opportunity for British chemists to show what they could do, and to prove beyond question their indispensable value to the nation. The way in which they rose to this opportunity and the feats which they accomplished would, if they had been foretold in the previous time of peace, have been regarded by chemists themselves as a wild impossibility. In the manufacture of explosives, and still more in the development of counter measures, both defensive and offensive, against the newer methods of warfare introduced by the enemy, the chemist held the key to the position. Chemists were required for work which only they could do in every section of the war organisation; with the special chemists' corps in the front line, to direct anti-gas measures and gas attacks, and, incidentally to identify the various poisonous compounds which the enemy sent over; with the R.A.M.C., to supervise water supply, etc.; in the Navy, to direct the manufacture and use of artificial fog; in the various munition factories; in the Government and other research laboratories; and in other activities too numerous to mention. It would be untrue, as well as grossly unfair to other workers and especially to our fighting forces, to claim that chemists won the war. But we have every right to claim that, had it not been for the work of the British chemists, we should inevitably have lost it.

* Presidential Address, delivered before Section B (Chemistry), of the Australasian Association for the advancement of Science at the Meeting held in Melbourne.

There is every indication that unless the League of Nations becomes an effective restraining force, chemistry will play an even greater part in future wars than it has in the one we have just come through. This has already been recognised in the United States, where the Chemical Warfare Service has been organised as an independent branch of the Army. It would seem therefore, that except in wars against savage or semi-savage tribes, the days of the "dashing cavalry general" are over, and that he will have to be succeeded by one whose training has consisted largely of chemistry and engineering. If both sides are prepared for it, chemical warfare does not add so much to the horrors of war as the use of high-explosive shell. In 1918, the number of casualties in the British Army from poison, sufficiently severe to incapacitate a man for some weeks was unfortunately very large, yet the number of deaths therefrom was estimated not to have exceeded 4 per cent, whilst the percentage of deaths from gunshot wounds was between 20 and 30. The special infamy committed by the Germans lay in their taking deliberate advantage of a solemn covenant not to use poisons to spring a ghastly surprise on their opponents. The effect of that first chlorine attack in Flanders in May, 1915, was devastating, and had it been followed up, might well have been decisive. Apparently nothing prevented the Germans from marching through to the Channel Ports but the same kind of mental inertia and suspicion of new inventions on the part of the German professional officer, said to be characteristic of his British colleague.

When they began the war, the German High Command believed that the stocks of explosives and other munitions which they had previously been accumulating would be sufficient to enable them to override all opposition. Hence in Germany as with us, the manufacture of explosives was at first organised sufficiently to meet only peace-time requirements. But as soon as it was found that the Allies had developed an annoying capacity to hinder the war from proceeding according to plan, both sides were faced with the necessity to extend the manufacture of explosives on an unheard of scale. In this, however, the Germans started with the advantage greatly on their side The enormous factories for the manufacture of dyes and other fine chemicals which had grown up in Germany were an invaluable asset, since the chemical plant which they contained could be converted rapidly to the purposes of explosives manufacture, and what is of some import at the present time, could as readily be re-converted to serve peace-time requirements. In Britain, on the other hand, the corresponding chemical resources were relatively small, so that we had to face the problem of erecting and equipping huge and entirely new factories, specially to meet the enormous demands suddenly made upon the nation. In response to these demands, there gradually arose that extraordinary organisation known as the Department of Explosives Supply of the Ministry of Munitions, with Lord Moulton as its Director-General. Lord Moulton's services to the nation have been frequently and justly extolled, but probably the greatest of them all was his selection for his Chief of Staff of Mr. K B. Quinan, of the Cape Explosives Works. Mr. Quinan came from South Africa with an established reputation as an explosives expert and chemical engineer. When he returned thither at the close of the war he had proved himself to be one of the greatest organisers and men of genius who had fought in the Allied cause. Whilst he never spared himself, he possessed in a high degree the gift of winning the confidence and getting the very best out of those around him It has happened to few men to receive such whole-hearted loyalty from colleagues and subordinates, and few have so well deserved it.

It was under Mr. Quinan in the Factories Branch of the Department of Explosives Supply that the British chemist found his greatest chance to come into his own. Starting from small beginnings in 1915, the Factories Branch gradually extended, until at the close of the war it controlled more than 20 factories, producing not only explosives, but also a great variety of other materials, including many of the so-called "poison gases." Many of these factories were designed by Mr. Quinan and erected under his supervision, and the management of all of them was subject to his control. Amongst the most noteworthy achievements were the great factory at Queen's Ferry, near Chester, capable of turning out over 800 tons per week of T.N.T., and over 200 tons per week of nitrocellulose, and the still larger factory at Gretna with a capacity of over 800 tons per week of finished cordite. Except that it obtained about half the necessary amount of nitrocellulose from Queen's Ferry, Gretna was self-contained, producing besides the balance of the nitrocellulose all the acids, ether and nitroglycerin it required. There was also a very large distilling plant for the refining of the crude glycerin.

Hand in hand with the erection of these factories had to go the training of the staffs to run them, and in this Mr. Quinan developed a two-fold purpose. The first consideration was of course to turn out the materials necessary for winning the war. (The possibility of losing it apparently did not trouble him). The second, however, was to make of the Department a great educational institution, and to give to the chemists and engineers who came under his influence such a thorough training in the erection and running of chemical plant and in all the details of factory management that they would be qualified to play their part in the great task of building up and extending the British chemical industries after the war was won. The methods by which these aims were accomplished are best described in Mr. Quinan's own words in the preface to the "Second Report on Costs and Efficiencies for H.M. Factories Controlled by the Factories Branch," dated September, 1918, and subsequently published by the Ministry of Munitions.

As was to be expected, the chemists showed themselves to be receptive pupils, and Mr. Quinan's educational policy met with complete success. The circulation of comparative costs data, combined with the frequent conferences between the staffs of the various factories and the Headquarters Staff of the Department, developed a spirit of emulation amongst the former, quite equal to that called up by severe trade competition. This, and the fact that they were provided with the very best plant obtainable, resulted in a smoothness and efficiency of working, which, all things considered, was little short of marvellous.

But the activities of the Department of Ex-

plosives Supply did not stop at explosives. Towards the end of 1917 orders were received to get out designs for a factory to produce about 30,000 tons per annum of synthetic ammonia for the immediate purpose of producing about 60,000 tons per annum of ammonium nitrate, but with the ultimate post-war object of making other ammonium compounds. After some two years' work, a team of ardent research chemists in the Munitions Inventions Department, including the late Dr. H. C. Greenwood, whose death about a year ago is so much to be deplored, had succeeded in reproducing the Haber process for the synthesis of ammonia on a large laboratory scale. The results which they had obtained were so promising, that Mr. Quinan decided to adopt the Haber process for the new factory. For war purposes, about half the ammonia so produced was to be oxidised by means of the Kuhlmann catalytic process to nitric acid, which in turn was to be neutralised with the balance of the ammonia. Although the designs were partly completed, various causes, notably the necessity to concentrate on the manufacture of poisons, prevented rapid progress from being made with the factory itself; and when the Armistice was signed, all work on the latter was suspended. The project has, however, since been taken over by a syndicate formed by Brunner, Mond & Co., and it is to be hoped that, as a measure of national safety, it will be carried to completion.

The history of the Haber process affords one of the most striking illustrations of the truth, that the most far-reaching discoveries in the domain of applied science are often the result of research carried out, not with a definite technical aim, but solely from a desire to advance knowledge. The conditions for equilibrium between hydrogen, nitrogen, and ammonia possess very considerable physico-chemical interest; but in the early stages of Haber's researches thereon, commencing in 1905, it would have been difficult to find any chemical reaction which looked less likely to become of technical importance than the direct synthesis of ammonia from its elements. Even under high pressure and with the most active catalysts so far discovered, the temperature has to be pushed so high to obtain a sufficient rate of reaction, that equilibrium is reached when only comparatively small fractions of the hydrogen and nitrogen have combined. The suggestion that this unpromising reaction might be utilised for the manufacture of ammonia on a large scale was first made by Le Rossignol, a native of Jersey, who had been trained in Sir William Ramsay's laboratory in London, and had subsequently gone to work with Haber. Le Rossignol's proposal was to circulate the gases continuously under pressure through the catalyst furnace, a heat exchanger, an ammonia absorber, and again through the heat exchanger to the furnace. To test this suggestion a small laboratory plant was constructed by Haber and Le Rossignol, the working of which was so satisfactory that in 1909 the invention was taken over by the Badische Anilin und Sodafabrik. The difficulties in the way of constructing and running a large scale plant to work at about 600° C., and under a pressure of 150 to 200 atmospheres were considerable, but were successfully overcome. In 1917, the factory erected by the Badische Company at Oppau produced 93,000 tons of ammonia, reckoned as pure $NH_3$, by this process, whilst a second factory at Merseburg, near Halle, has twice that capacity. Besides the Haber process, the Germans were also using the cyanamide process and the Pauling arc process for producing synthetic nitrogen compounds; but of the three the Haber process has proved itself to be the most economical and important. Had it not been for these processes, the Germans would have rapidly run short of nitrogen compounds both for agriculture and for the manufacture of munitions, and could hardly have survived one year of war. Perhaps this lesson is not entirely without interest for Australia.

(To be continued.)

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

*Ordinary Meeting, April 21, 1921.*

PROF. C. S. SHERRINGTON, President, in the Chair.

THE following papers were read:—

"*A Quantum Theory of Colour Vision.*" By PROF. J. JOLY, F.R.S.

According to the quantum theory of vision, the liberation of electrons in a sensitiser in the percipient layer of the retina is the source of vision, the energy values of the quanta proper to the three fundamental colours determining the sensation of colour.

In this paper the view is advanced that in accordance with the physiological law of nerve impulses, known as the "all-or-none" law, the cone is connected with the optic nerve through a plurality of nerve fibres; the rod being connected through one fibre only. This is supported by histological evidence.

The fundamental colour-sensations—red, green, and blue—may be taken as corresponding to frequencies in the ratio 2 : 3 : 4, and this is the ratio of the energies of the corresponding quanta and of the kinetic energies of the electrons liberated thereby. It is supposed that this is also the ratio of the numbers of fibres activated in the cone. In the case of the rod, quanta, in all cases, can activate but one fibre; hence its achromatic functions. In the case of the cone the activation of 2, 3, or 4 fibres evokes the fundamental sensations. White sensation arises when all nine fibres are activated.

The bearing of these views on the significance of the experimentally determined colour sensation curves and on colour blindness is considered. The energy relations of colour sensation and of luminous sensation are discussed.

"*The Energy involved in the Electric Change in Muscle and Nerve.*" By Prof. A. V. HILL, F.R.S.

An expression is given for the heating effect, in a muscle or nerve, of the currents produced by the electric response accompanying the propagated impulse. In a muscle the heat produced is not more than one hundred thousandth part of the energy liberated in a twitch; in a nerve it of the order of size of $3{\cdot}5 \times 10^{-10}$ calorie or $0{\cdot}15$ erg. per

grm. It is concluded from the smallness of these quantities, that no appreciable provision of energy is required in the propagation of the electric response, and that the physico-chemical change producing the response is the only factor involved in the propagated nervous impulse.

"*Asymmetry, Metamorphosis, and Origin of Flat-Fishes.*" By H. M. KYLE.

The flat-fishes owe their change of form in the beginning to an inherent asymmetry of the abdominal organs, the coil of the gut; the air-bladder is also asymmetrically placed. The vertebral column, spines, and fins develop asymmetrically according to the balance. Persistent flexures convey the asymmetry to the skull; the intermediate structures, urohyal, arches, jaws, cheek-muscles, showing distorsion and rupture. The basal axis of the skull is flexed to one side, the frontals to the other; the migration of the eye is the final event in a long series of causes and effects.

Many normal Teleosts form a coil and display the same initial disturbances, but their balance is less defective and the skull escapes deformity in various ways; *e.g.*, the body flexures are damped by means of spinous rays, the abdominal cavity is not enclosed by asymmetrical structures, the skull is so strongly depressed that the jaws operate on the dorsal surface, or the jaws operate solely on the head of the vomer.

The metamorphosis being due to defective balance takes place during the pelagic stages; the fish swims and lies on one side because that side becomes the heavier; the side to become the heavier varies according to the balancing organs. After the demersal habit has been attained, changes in fundamental structure are improbable. Hence, essential differences indicate separate origins. The flat-fishes have appeared in phylogeny, that is, the skull became affected by the asymmetry of the body, when the coil of the gut was forming and when the caudal region came to occupy more than half the total length. Nearest the beginning stands the large family of Cynoglossids with intermediate Teleostean characters; at the other end is Psettodes, an isolated species, with advanced characters; between these lie several groups. Confirmation of this view is found in the affinity of each group to separate types of normal Teleosts ranging from the Macrurids to the Percoids.

"*Studies in the Cytology of the Statolith Apparatus in Plants, viewed in Relation to their Habit and Biological Requirements.*" T. L. PRANKERD.

Part I. deals with the reaction to external stimuli of some Liverworts and demonstrates that the degree of geotropic irritability corresponds in general with the biological requirements of the plant. It is further shown that the statolith apparatus is also gradational in its expression, *i.e.*, it is usually absent in vegetative thalli where position is of no importance, while it is most strikingly developed in the strongly geotropic gametophores and sporogonia.

Part II. describes the movements executed by fern fronds in response to internal and external stimuli. In a study of some 15 species (representative of the Filicales) geotropic irritability was always present, though both latent and reaction times are greater than the corresponding periods for Angiosperms. A cylinder of statocyte tissue is always developed in the ground tissue of the young rachis, which disappears at about the time of unfolding of the leaflets, when response to gravity also ceases. Detailed work on *Asplenium bulbiferum* shows that a curve expressing the rise and fall in the amount of statocyte tissue present corresponds more closely with the curve of geotropic irritability than with those of heliotropism, epinasty, or growth. It is interesting to note that growth continues some time after the simultaneous loss of the statolith apparatus and the power of gravitational response.

The most important points in this investigation are:—

(1) The demonstration of geotropic irritability in fern fronds, and the physiological evolution implied in the relatively long latent and reaction periods;
(2) The close correlation of this irritability with the development of a statolith apparatus;
(3) The varied types of statocyte occurring in the Filicales, including the "nucleostatolith" of Angiopteris and the curious swing mechanism of Gleichenia.

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*Ordinary Meeting, April* 28, 1921.

PROF. C. S. SHERRINGTON, President, in the Chair.

THE following papers were read:—

"*Vibrations of a Spinning Disc.*" By Prof. H. LAMB, F.R.S., and R. V. SOUTHWELL.

This investigation was suggested by the occasional failure of the blades of steam turbines, apparently resulting from flexural vibrations of the turbine disc. For practical purposes it will be necessary to calculate the frequencies natural to discs of tapering profile; but the present discussion, which is confined to discs of uniform thickness, illustrates the physical aspects of the problem. The decision to publish a joint paper was reached when it was discovered that both authors had attacked the problem independently, and that their methods and results were closely parallel.

Expressions have been obtained for the gravest natural frequencies of vibration—(1) by exact methods, on the assumption that the disc is so thin, or rotates so fast that the restoring effects of centrifugal force are predominant, and the effects of flexural rigidity negligible; (2) from Kirchhoff's theory for flat circular plates, in cases for which the opposite assumption can be made; and (3) by Rayleigh's approximate method, employing an *assumed* curve of deflection, for cases in which both centrifugal and flexural effects require to be taken into account.

The problem is of theoretical interest, as an example of vibrations in which two distinct systems of restoring forces act simultaneously. A theorem due to the late Lord Rayleigh shows that the results of employing method (3) above must be to *over-estimate* the gravest natural frequency of vibration. As an extension of the same theorem, it is here shown that a corresponding *lower limit* can be obtained by considering each restoring system separately. In the most important case of the problem treated, the upper and lower limits deduced in this way differ by litle more than 1 per cent; the lower limit is the easier to obtain.

"*The Hardness of Solid Solutions.*" By Dr. W. ROSENHAIN, F.R.S.

It is suggested that crystals of a solid solution of metal B in metal A are built up on a single space lattice system similar to that of crystals of pure A, but that certain atoms of A on this space lattice are replaced by atoms of B. As the atoms of B are necessarily somewhat dissimilar from atoms of A, this replacement involves a certain amount of distortion of the space lattice, *i.e.*, atoms of A in the neighbourhood of an atom of B will be pulled or pushed slightly out of their normal position. The amount of such distortion will depend upon the degree of dissimilarity between the two kinds of atoms. If the atoms are sufficiently dissimilar, the distortion will be considerable, and consequently the number of atoms of B which can be introduced into the space lattice of A will be limited. At the same time, the mechanical properties of the crystals will be affected by the slight distortion of the space lattice arrangement, surfaces which were plane gliding surfaces in the crystals of pure A being no longer perfectly plane in the solid solution crystals, and consequently offering an increased resistance to slip within the crystal.

It follows that the greater the distortion introduced into the space lattice by the introduction of an atom of B, the greater will be the hardening effect of the introduction of B into A in the form of solid solution. This leads to the inference, as a rough first approximation, that the hardening effect of one metal upon another in solid solution is inversely proportional to the solubility of that metal in the first. This inference is shown to be in accordance with fact in regard to the alloys of various metals, particularly those of copper with nickel, manganese, zinc, aluminium, and tin respectively; and it is suggested that the law is in general conformity with the known facts concerning the majority of alloys.

"*A Method of Analysing Galvanometer Records.*" By W. HARTREE and Prof. A. V. HILL, F.R.S.

The motion of a galvanometer connected to a thermopile in contact with a body producing (or absorbing) heat is governed by linear differential equations with constant coefficients, and it is possible, from the relation between galvanometer deflection and time, to determine the relation between heat-production and time. It is necessary to construct a "control curve," *i.e.*, the relation between galvanometer deflection and time for an instantaneous liberation of heat in the body on the thermopile. The observed curve may then be reconstructed in terms of the control curve, and employing a numerical method described in the paper, it is possible to make a fair analysis of the course of the production (or absorption) of heat.

"*A New Form of Wehnelt Interrupter.*" By F. H. NEWMAN.

1. The new form of electrolytic interrupter consists of a platinum wire immersed in a saturated solution of ammonium phosphate. The whole is contained in an aluminium vessel, which acts as the cathode.

2. The current density at the anode is only one-quarter of the value in the old form of Wehnelt Interrupter. Consequently there is less heating of the electrolyte, and less disintegration of the platinum wire.

3. The interrupter can be used with alternating currents, which it rectifies.

4. The secondary discharge, obtained from the new type of interrupter, is very disruptive. It has a large peak value.

5. This modified type of interrupter works without self-induction in the circuit, when used with alternating currents.

6. The primary current wave form has been investigated with direct and alternating currents.

"*Some Experiments on Thermal Diffusion.*" By T. L. IBBS.

The experiments were made with the object of investigating experimentally some of the conclusions relating to thermal diffusion, arrived at by Dr. S. Chapman in his Kinetic Theory of Gases, thus extending the experimental work of Chapman and Dootson. The method employed is new, and depends on the use of the katharometer as an instrument for accurate gas analysis. A temperature gradient was applied to a number of mixtures of hydrogen and carbon-dioxide by passing them through a cylindrical glass tube, down the middle of which was a platinum helix. The helix was heated to different temperatures by an electric current. A steady flow of the gas mixture was maintained, and the gases were drawn off from the hot and cold regions of the tube, subsequently passing through a differential katharometer for analysis. The results showed that there was a general tendency for the hydrogen to diffuse towards the hotter region, and the carbon dioxide towards the cooler region, thus confirming the results of Chapman and Dootson. The experiments also show clearly the effect of variation of the temperature gradient on the amount of separation obtained. Curves are drawn showing that the amount of separation is proportional to Log $\frac{T_1}{T_2}$ where $T_1$ and $T_2$ are the absolute temperatures of the hot and cold regions. The experiments also show that the greatest amount of separation for a given temperature gradient is obtained in mixtures containing from 50 to 60 per cent by volume of hydrogen. The nature of the results gives strong support to the theory worked out by Chapman. The amount of separation is less than would be expected if gas molecules behaved like rigid elastic spheres.

"*Diffraction of Light incident at nearly the Critical Angle on the Boundary between Two Media.*" By B. N. CHAKRAVARTY.

# CORRESPONDENCE.

## ESTIMATION OF PHOSPHOROUS IN PHOSPHOR BRONZE.

*To the Editor of the Chemical News.*

SIR,—The following modification in the estimation of phosphorus in phosphor bronze may be of interest, and many of the details are, I think, new. The following method does away with the necessity of having to fuse the stannic oxide residue which contains the phosphorus present, and is a simple, clean, and above all, accurate method, and can easily be completed in under one hour. The details given below have worked satisfactorily.

To 1 grm. of the alloy 0·5 grm. either iron wire,

or mild steel turnings is added. The mixed metals are taken into solution with 15 cc. aqua regia (5 cc. $HNO_3$ : 10 cc. HCl). When solution is effected, boil for a few minutes, cool, and nearly neutralise with AmOH. Sufficient $K_2Mn_2O_8$ is then added, so that a distinct precipitate persists on boiling for two minutes. This is cleared with a few drops HCl. The solution is then cooled and diluted somewhat, and the basic ferric phosphate precipitated with 25 cc. AmOH (0·880 sp. gr.). The precipitate is gradually taken into solution, using strong $HNO_3$. This should be added from a burette, in order that the neutral point may be obtained. This is easily recognised, being a dark-coloured liquid, free from suspended precipitate. An excess of 3 cc. $HNO_3$ is then added, the liquid clearing to a bright apple-green solution. This is then brought to the boiling-point, removed from the flame, and the phosphorus present precipitated by the addition of sufficient nitro-molydic reagent.

The precipitate is allowed to stand at room temperature for at least 20 minutes, and is then filtered, washing in the first place with 2 per cent $HNO_3$, and then washing free from acid with 2 per cent. $KNO_3$. The phosphorus present is determined by dissolving the precipitate in an excess of std NaOH, the excess being estimated with std. $HNO_3$. Using phenolphthalein as an indicator. The solutions are standardised against a steel with a known phosphorus content. The small amount of Phosphorus in the added iron or steel must of course be deducted.—I am, &c.,

GEO. GREENWOOD.

99, The Grove,
Ealing, W.5.

## BOOKS RECEIVED.

"Tables of Refracted Indices. Vol. II.—Oils, Fats, and Waxes." Compiled by R. KANTHACK. Edited by J. N. GOLDSMITH. 292 pages. London: Adam Hilger, Ltd. Price 25s. net.

"Clayworkers' Handbook." A Manual for all engaged in the Manufacture of Articles from Clay By ALFRED B. SEARLE. 381 pages. London: J. J. Griffin & Sons. Price 21s. net.

"Coke Oven and By-Product Works Chemistry." By THOS. BIDDULPH-SMITH. 62 illustrations. 7 folding plates. 180 pages. London: J. J. Griffin & Sons. Price 21s. net.

"Technical Methods of Analysis as Employed in the Laboratories of the Author." By D. LITTLE, Inc. Cam. Mass. Edited by ROGER CASTLE GRIFFIN. First Edition. New York and London: McGraw-Hill Book Co., Inc.

"Animal and Vegetable Fixed Oils, Fats, Butters, and Waxes: Their Preparation and Properties, and the Manufactures therefrom of Candles, Soap, and other Products." By C R. ALDER WRIGHT. 3rd Edition. Revised and greatly enlarged by AINSWORTH MITCHELL. 3 plates and 185 illustrations. 939 pages. London: J. J. Griffin. Price 56s. net.

"Metallic Alloys: Their Structure and Constitution." By G. H. GULLIVER. Fourth Edition with Appendix. 332 illustrations. xxvii.+439 pages. London: J. J. Griffin. Price 15s. net.

"A Primer on the Storage of Petroleum, Spirit, and Carbide of Calcium: For the Use of Local Inspectors and Motorists." By MAJOR A. COOPER KEY. Second Edition. x.+132 pages, with Appendix. London: J. J. Griffin. Price 5s. net.

## NOTES.

ROYAL INSTITUTION.—A General Meeting of the Members of the Royal Institution was held on the 9th inst., Sir James Crichton-Browne, Treasurer and Vice-President in the Chair. Mr. W. E. Watson Baker, Dr. R. Langdon Downe, Mr. R. W. Paul, Mr A. S Tabor, and Mrs. S. S. Williams were elected Members. Sir J. J. Thomson was elected Honorary Professor of Natural Philosophy, and Sir Ernest Rutherford Professor of Natural Philosophy.

ROYAL INSTITUTION.—On Tuesday next, May 17, at 3 o'clock, Mr. E. Clodd gives the first of two lectures at the Royal Institution, on the "Origin and Development of Occultism." Owing to the illness of Dr. MacColl, the lectures on Thursdays May 19 and 26 will now be delivered by Mr. Ernest Law on "The Architecture and Art of Hampton Court Palace." On Saturday, May 21, Mr. F. Legge begins a course of two lectures on "Gnosticism and the Science of Religions." The Friday Evening Discourse on May 20 will be delivered by Dr. E. H. Starling on the "Law of the Heart," and on May 27 by Mr. A. Mallock on "Elasticity."

WE have received a copy of the "Directory of Paper Makers" for 1921 from Messrs. Marchant, Singer, & Co. The Directory is very complete, and contains all the information likely to be needed by printers, stationers, publishers, and all users of paper. A complete list of watermarks is given, by which it is possible to identify the maker of any water-marked paper, and the list of trade customs gives very useful information to anyone dealing in paper. A list of paper-makers, &c., in the United Kingdom, has been revised and brought up to date. Price 2/9 net, post free in the United Kingdom

## New Patents.

THIS List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W.C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

11646—Alby United Carbide Factories, Ltd.—Manufacture of salts of guanidine. April 22nd.

11553—Buchler, H.—Process of production of boro-di-salicyclic acid. April 21st.

11766—Callimachi, M T.—Manufacture of threads, filaments, etc, of cellulose. April 23rd.

11311—Calorizing Corporation of America.—Mettalis alloys. April 19th.

11771—Courtaulds, Ltd.—Manufacture of carbonbisulphide. April 23rd.

*Specifications published this Week.*

161591—Weizmann, C. and Legg, S. A.—Manufacture of secondary butyl alcohol.

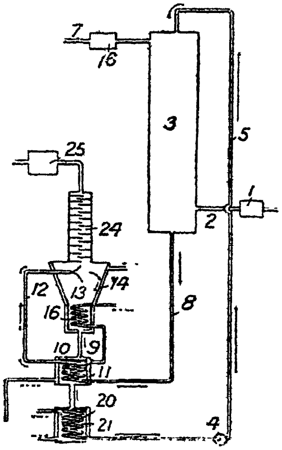
117085—Deutsche Gold-und-Silber Scheide Anstalt vorm. Roessler.—Manufacture of alkali percarbonates.

161656—Mackay, P. A.—Process of obtaining copper sulphate direct from metallic copper.
147583—Still, C.—Method of purifying coal gas by means of ammonia.

*Abstracts Published this Week.*

Mr. G. C. Claude of 48 Rue Saint Lazare, Paris, has obtained a Patent No. 158593 in this country for improvements to the protecting of the walls of the enclosure in which an exothermic reaction is carried out under high pressure and at a high temperature, for instance, the synthesis of ammonia using "hyperpressures" according to Specification 130086. A layer of molten material interposed between a chamber in which the reaction takes place and a pressure sustaining wall, is, by selection of bad thermic conductivity, neutral with respect to the bodies present, and of low vapour tension, suitable materials are a metallic chloride, caustic soda or potash, a eutectic mixture of the latter, and borax dissolved in boric acid. To prevent transmission of heat by convection, the molten material may be held stationary by the addition of solid material of bad thermic conductivity, such as sand, coke, powdered magnesia, or magnetic oxide of iron, employed in a granular or pulverulent state in such a manner as to form a paste or pulp. Substances such as litharge may be added to the molten material to absorb hydrogen, etc., that may become dissolved therein and which might attack the wall of the enclosure. In the apparatus, the catalyst is contained in the inner tube, surrounded at the lower part by an electrical heating-device, and the reaction gases enter at the connection, pass through the annular or helical space between the tubes, then traverse the catalyst, where they are brought to reaction, and finally escape through the connection. At the point where the gases enter, the temperature is insufficient to lead deterioration of the wall, and it is adequate to continue the molten material to a height at which the temperature ceases to become injurious to the wall. Several layers of liquids may be employed, the more fusible at the top and extending down to a level, and the less fusible from other levels, such viscous liquid may consist of boric acid containing an increasing proportion of borax.

*Sulphur Dioxide.*—Mr. P. Pascall of 117, Boulevard Hausmann, Paris, has been granted a Patent No. 159337 for a new process of obtaining sulphur dioxide from dilute gas mixtures. For instance gases from the roasting of blende and pyrates by treating the gas mixture under pressure with carbolic oil obtained by distilling coal tar at 175-225°C., and separating the dissolved gas by heat and reduced pressure, after which the gas is liquefied. The dilute gas is compressed by a compressor 1 and delivered by a pipe 2 to a packed tower 3 supplied with oil by a pump 4 through a pipe 5. The issuing gas is expanded in an expander 6 and led by a pipe 7 to apparatus for recovering the last traces of sulphur dioxide. The oil passes from the bottom of the tower 3 by a pipe 8 to a coil 9 in a heat exchanger 10 having a jacket 11 supplied with steam and then it is delivered by a pipe 12 in a tangential jet into an expanding chamber 13 having a steam jacket 14. The oil collecting in the lower part of the expander 13 is heated by a steam coil 16, from which the steam passes through the jacket 11 of the exchanger 10. The oil from the expander 13 passes through the exchanger 10 through a coil 20 in a cooler 21 and thence to the pump 4. The sulphur dioxide separated in the expander 13 passes up a plate tower 24, which separates oil vapour, to a suction pump 25 after which it is liquefied.




Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

THE CHEMICAL NEWS.
VOL. CXXII., No. 3188.

## FRACTIONAL DISTILLATION WITH CONTACT RING STILL-HEADS.*

By Dr. R. LESSING.

THE author draws attention to the advantages of packing absorption towers and distilling columns with contact rings of the type described in his Brit. Pat. No. 139,880. These rings consist of cylinders of approximately equal height and diameter, having a gap in the circumference and a more or less diametrical partition connected on one side with the cylinder, but out of touch on the opposite side. They are disposed indiscriminately in the tower or column at the angles which they find when dropped promiscuously into a vessel. The provision of the central partition and openings has been found to increase the efficiency of this packing over Raschig rings by increasing the contact surface available in a given tower space and the drainage capacity.

The standard rings of 1in. diameter by 1in. height are used in a great variety of plants of the chemical and gas industries, amongst which may be cited ammonia scrubbers, absorbers, washers, tar extractors, carbolate decomposers, carbonating and decarbonating towers, debenzolising stills, distilling columns and still-heads for many substances such as tar and petroleum products, alcohols and essential oils, condensers, coolers, heat exchangers, and are applicable wherever large interfacial surface for liquid and gas or vapour, combined with a minimum of back pressure is essential.

Smaller sizes of Lessing contact rings down to ¼in. diameter are now available, and are particularly useful for the construction of laboratory still-heads on the lines on which the larger rings are applied in manufacturing operations. They have a surface of 8250 sq. cm. per litre (251 sq. feet. per cubic foot), and only occupy 13 per cent total space, leaving 87 per cent of free space for vapour and condensate. The resistance of such still-heads is almost negligible and they can therefore be made of considerable height.

They are simple in construction, and the rings can be transferred from one column to another, or be used in absorption towers or reaction vessels, and are therefore of general applicability. They have a remarkable fractionating efficiency, and are in this respect superior to other dephlegmators. This efficiency is due to the large surface per unit of volume, the turbulence created by frequent deflection of currents of vapour and condensate, and the consequent absence of channeling.

In order to obtain the maximum efficiency, the author recommmends lagging or even heating of the still-head to avoid undue condensation, and to provide a reflux condenser, or to use a definite length of the still-head itself as reflux condenser. Thus, return flow and irrigation of the whole length is obtained. A ring packed still-head may then be regarded as a scrubber in which the ascending vapours are scrubbed with the descending condensate.

Still-heads can be constructed from plain glass tubes or metal pipes by merely dropping the rings into them.

The paper contains a number of graphs proving the efficiency of fractionisation obtainable. From a mixture of equal portions of benzene and toluene 47 per cent of benzene distilled within less than 1°, and a like portion of pure toluene was yielded, leaving only about 5 per cent of the total volume in the mixed middle fraction.

From a crude coke oven benzol, almost all the benzene and toluene could be distilled off each within 0·2° C., although the sample contained 30 per cent of naphthalene and wash oil. The effect of still-head dimensions, heat insulation and reflux condensing is shown in one set of curves. Another chart deals with the distillation of fusel oil, and a remarkably sharp separation of the various higher alcohols from each other and from water is shown in a further graph. The fractionating effect is so sharp that chemically anhydrous alcohol may be in the lower part of the still-head, while there is sufficient water in the upper portion to separate as a distinct layer from the distillate.

* Read at the Meeting of the London Section of the Society of Chemical Industry, Monday, May 2, 1921.

## METHODS FOR THE COMPLETE RECOVERY OF NITRE CAKE.*

By W. H. H. NORRIS, B.A., B.Sc.

PREVIOUS to 1915 the utilisation of nitre cake in this country was on a comparatively small scale. During the war over 80 per cent of the considerably increased production was employed, but largely by methods which completely wasted the sodium sulphate contents. With ample supplies of sulphuric acid, only those methods of recovery will stand which are economically sound, and the production of by-product salt cake in a pure and marketable form will assist in this direction.

Processes of war expediency may be passed over. The oldest method for complete recovery was by the salt cake furnace, and this well-known operation calls for little comment. Expenditure on hard coke at present prices is a considerable charge, and where hydrochloric acid is the valuable product, nitre cake has little chance of competing with sulphuric acid because of the reduced yield per furnace, and the impurity of acid produced when nitre cake is employed.

Many other methods have been suggested, but the writer does not know that any of these have been carried out on a manufacturing scale with the exception of the following.

Nitre cake may be used for ammonia absorption producing sulphates of ammonia with the additional formation of sodium sulphate suitable for glass makers.

A process was described which has been worked out in conjunction with H. S. Denney and C. W. Bailey, and 220 tons of nitre cake used to produce 157 tons of salt cake and 87 tons of ammonium sulphate by it. The plant was run in conjunction with a Mond Gas Ammonia Recovery Plant, and proved successful in operation, process figures and costs for which were given.

The method is of wide application and may be used either with ammonia absorption towers and

* A paper given before the Manchester Section of the Society of Chemical Industry, May 6th, 1921.

dasher washers or in the ordinary saturator as employed on coke oven and gas works liquor recovery plants. The operation works up all its own waste liquors, and requires the minimum of handling and evaporation.

Briefly, the nitre cake is digested with hot process liquor, and the whole of its contents of salt cake are precipitated in a pure form, while all the acid is taken into solution. The mixture is filtered, and washed in centrifugals, and the acid liquor resulting used for ammonia absorption, in the saturator or other absorption plant. The neutralised liquor is evaporated in the usual way, for the deposition of sulphate of ammonia containing over 24 per cent free ammonia, but concentration is checked when a definite density is reached, and the process liquor run back to the digester to extract the acidity from a fresh charge of nitre cake.

## THE SEPARATION AND DETECTION OF ARSENATE AND ARSENITE.

By, GEO. W. SEARS.

Of the methods now available for the detection of arsenate and arsenite those based on the formation of arsine (*Chem. Ztg.*, xxxiii., 1209; *Z. anal. Chem.*, 1902, xli., 362) and those taking advantage of the oxidising power of arsenates (*Am. J. Sci.*, [3] 1894, xlviii., 216) or the reducing power of arsenites (*ibid.*, [4] 1896, 1., 35) are perhaps the most common. The limited applicability of these methods to a general separation and detection of the more common acid radicals led the author to make a study of the relative solubility of their silver salts in various concentrations of sodium hydroxide. When silver arsenite, to which potassium hydroxide has been added, is allowed to stand in the sunlight or is heated to 50° on the water-bath, the arsenic slowly dissolves with the formation of potassium arsenate (*Ber.*, 1894, xxvii., 1019). No information, however, was available regarding the effect of alkaline solutions other than ammonium hydroxide, on silver arsenate. Both salts are readily soluble in ammonium hydroxide ("Dictionary of Chemical Solubilities, Comey, pp. 37-42). An examination of the two salts with respect to their relative solubility in excess of sodium hydroxide leads to a study of the following equilibria.

$$2Ag_3AsO_4+2NaOH+H_2O \rightleftarrows 2NaH_2AsO_4+3Ag_2O \quad (1)$$

$$2Ag_3AsO_3+2NaOH \rightleftarrows 2NaAsO_2+3Ag_2O+H_2O \quad (2)$$

$$2Ag_3AsO_3+6NaOH \rightleftarrows 4Ag+Ag_2O+2Na_3AsO_4+3H_2O \quad (3)$$

### *Experimental.*

*Preparation of Silver Arsenate and Silver Arsenite.*—Weighed amounts of the C. P. sodium salts were dissolved in enough water to make a concentration of 10 mg. of the acid radical per cc. of solution. Definite volumes of these solutions were diluted, acidified with nitric acid and an excess of silver nitrate was added. To the resulting mixture sodium hydroxide was added drop by drop with constant stirring until the black precipitate of silver oxide just failed to redissolve. The appearance of the black silver oxide is very definite and easy to detect, and hence makes a very satisfactory indicator. Under these conditions the solution has an acidity of about $10^{-5}$ to $10^{-7}$. It reacts acid toward phenolphthalein and basic toward methyl orange. With congo red an orange to violet colour is obtained. Both silver arsenate and silver arsenite are completely precipitated, and can be filtered with ease. (The filtrate does not give a precipitate with $H_2S$.) The salts obtained in this way and containing a definite weight of the acid radical were removed from the filter by means of a fine stream of water. This resulted in a rather finely divided suspension to which the solvent was added.

*Solubility of Silver Arsenite.*—Approximately 6 *N* sodium hydroxide solution was added to the precipitate of silver arsenite suspended in 10 to 20 cc. of water as indicated above, and after a thorough mixing, the mixture was filtered and both precipitate and filtrate tested for arsenic as follows. The precipitate was leached with 6 *N* hydrochloric acid to dissolve the arsenic and remove the silver. The clear solution was then saturated cold with hydrogen sulphide. The filtrate was strongly acidified with hydrochloric acid and saturated with hydrogen sulphide. Table I. shows the behaviour of silver arsenite toward various concentrations of sodium hydroxide. The residue invariably gave a positive test, and the filtrate a negative test, except in the last experiment, when the filtrate gave a positive test.

Table I.

| Mg. $AsO_3'''$. | Cc. of Approx. 6 *N* NaOH | Total volume cc. | Approx. normal strength. |
|---|---|---|---|
| 0·5 | 0·2 | 10 | 0·12 |
| 1 | 0·2 | 10 | 0·12 |
| 10 | 0·2 | 10 | 0·12 |
| 100 | 0·2 | 10 | 0·12 |
| 0·5 | 0·5 | 10 | 0·3 |
| 10 | 0·5 | 10 | 0·3 |
| 100 | 0·5 | 10 | 0·3 |
| 0·5 | 1 | 25 | 0·24 |
| 100 | 1 | 25 | 0·24 |
| 1 | 2 | 25 | 0·48 |
| 1 | 5 | 25 | 1·2 |
| 50 | 5 | 20 | 1·5 |
| 50 | 5 | 15 | 2 |

The results obtained show that cold sodium hydroxide up to about 1·5 *N* has no solution effect on silver arsenite, though higher concentrations seem to have a slight solvent action. In Reichard's work (Reichard, *Ber.*, 1894, xxvii., 1019) on the action of potassium hydroxide on silver arsenite no statement is made regarding the concentration of potassium hydroxide solution used, hence it seemed advisable to repeat a part of his work, using small concentrations of sodium hydroxide solution. The results obtained from a number of experiments showed that at the temperature of the water-bath silver arsenite is slowly dissolved in 0·5 *N* sodium hydroxide solution. The reaction proceeds almost entirely according to Equation 3 above, as shown by the fact that only a trace of arsenic could be detected by precipitation with hydrogen sulphide from a cold hydrochloric acid solution, while a considerable amount of metallic silver was left in the

residue. On the other hand, when the mixture was kept cold no reaction was detected in concentrations of sodium hydroxide below 1·5 $N$ and in higher concentrations (4-6 $N$) reaction according to Equation 2, seemed to predominate, although the presence of small amounts of metallic silver in the residue showed that some arsenic was dissolved according to Equation 3. Even in 6 $N$ sodium hydroxide solution only a small fraction of the silver arsenite present was dissolved.

*Solubility of Silver Arsenate.*—In the investigation of the solubility of silver arsenate experiments were carried out in the same manner as those with silver arsenite except that the residue after leaching with hydrochloric acid was heated to boiling before saturating with hydrogen sulphide. The filtrate was acidified with acetic acid and the arsenate precipitated with uranyl acetate The resulting uranyl arsenate was then dissolved in hydrochloric acid and arsenic precipitated with hydrogen sulphide as before. Preliminary experiments showed that some silver arsenate dissolved even in very small concentrations (0·05 to 0·1 $N$) of sodium hydroxide but seemed to indicate incomplete solution when as much as 5 mg. of the arsenate radical was present. With 0·5 to 1 mg. of arsenate, solution was complete as shown by a negative test on the residue and a positive test in the filtrate. When 50 to 100 mg. was used a considerable proportion seemed to dissolve, but in all cases the residue gave a positive test. Increasing the concentration of the sodium hydroxide made very little change in these results, while increased dilution of the arsenate seemed to give a greater solution effect. (Later work showed that these results were due in large measure at least to insufficient washing of the silver oxide residue).

The result of preliminary experiments indicated that an equilibrium was established in which perhaps 75 to 80 per cent of the arsenate was dissolved. It seemed worth while, therefore, to make a more careful study of the equilibrium

$$2Ag_3AsO_4+2NaOH+H_2O \rightleftarrows 2NaH_2AsO_4+3Ag_2O$$

in order to find out if possible the conditions under which it might be shifted to the right and complete solution of the arsenate be obtained. To this end several experiments were carried out as described above.

TABLE II.

| $AsO_4'''$. Mg. | Cc. of approx. 6 $N$ NaOH | Total volume cc | Approx. normal strength | Residue |
|---|---|---|---|---|
| 0·5 | 0·3 | 10 | 0·18 | Neg. |
| 1 | 0·3 | 10 | 0·18 | Neg. |
| 1 | 0·25 | 25 | 0·06 | Neg. |
| 10 | 0·5 | 25 | 0·12 | Neg. |
| 25 | 0·5 | 25 | 0·12 | Pos. |
| 50 | 1 | 25 | 0·24 | Neg. |
| 100 | 1 | 25 | 0·24 | Neg. |
| 150 | 1 | 25 | 0·24 | Pos. |
| 150 | 2 | 25 | 0·48 | Neg. |
| 200 | 2 | 25 | 0·48 | Neg. |
| 250 | 2 | 25 | 0·48 | Pos. |
| 400 | 3 | 25 | 0·72 | Neg. |
| 450 | 3 | 25 | 0·72 | Neg. |
| 1 | 0·13 | 25 | 0·03 | Pos. |

Various concentrations of sodium hydroxide were added to the precipitate of silver arsenate, suspended in water, and the mixture was well stirred before filtering. The silver oxide residue was then washed till the wash water gave no further test for alkali with litmus paper.

Table II. shows the behaviour of silver arsenate toward various concentrations of sodium hydroxide. The filtrate gave a positive test in every experiment except the last, which was negative.

It may be seen from the above results that the solvent action of sodium hydroxide on silver arsenate increases very rapidly with increasing concentration, and is appreciable at concentrations as low as 0·06 $N$. No action is apparent, however, in 0·03 $N$ sodium hydroxide solution.

*Discussion.*

From the foregoing results it is evident that a quantitative separation of arsenate and arsenite may be obtained by the action of sodium hydroxide solution (0·5-1·5 $N$) on their silver salts, the arsenate passing into solution. Higher concentrations of sodium hydroxide react slowly with silver arsenite with the formation of a mixture of soluble trivalent and pentavalent arsenic, probably according to Equations 2 and 3 above. Even very high concentrations, however, seem to have but slight solvent action in the cold.

It would seem, therefore, that some influence other than is apparent in the equilibrium represented by Equation 1 must come into action to affect the solution of silver arsenate since similar forces seem to act in the opposite direction in Equation 2. A compound of the formula $(As_2O_5)_2.3NaOH$ has been described by Filhol and Senderens as being formed by the action of excess sodium hydroxide on arsenic acid (Filhol and Senderens, *Compt. Rend.*, 1881, xciii., 388). They obtained it crystalline form only after evaporation to a syrupy consistency. No evidence of a similar action with arsenious acid was found. This difference in tendency toward complex formation with sodium hydroxide may, therefore, account for the difference in solubility of the silver salts. Without the formation of a complex ion the equilibrium represented in Equation 1 should shift toward the less soluble silver salt as is apparently the case in Equation 2.

*Procedure.*

(1) *Precipitation.*—To a nitric acid solution of the acids containing an excess of silver nitrate add sodium hydroxide drop by drop from a pipet until on shaking the dark silver oxide precipitate just fails to redissolve. Filter, wash the precipitate and transfer it to a graduate cylinder by means of 15 to 20 cc. of water from a wash bottle. Add 2 to 3 cc. of approximately 6$N$ sodium hydroxide solution and fill up to the 25 cc. mark with water. The amount of sodium hydroxide that should be added depends on the quantity of arsenate present. More than 450 mg. of arsenate is completely dissolved in 25 cc. of solution containing 3 cc. of 6 $N$ sodium hydroxide solution while as much as 5 cc. of the alkali in 25 cc. of solution produces no solvent action on the arsenite. Transfer the contents of the cylinder to a beaker and mix thoroughly. Filter, and wash the residue free from alkali. Test the residue for arsenite and the filtrate for arsenate.

(2) *Detection of Arsenite.*—Dissolve the residue of silver arsenite (1) by pouring a 5-cc. portion of 6 $N$ hydrochloric acid repeatedly through the filter and add hydrogen sulphide to the clear solution obtained. If a dark precipitate is obtained show-

ing the presence of heavy metal sulphides insoluble in hydrochloric acid, it may be tested for arsenic according to the usual methods.

(3) *Detection of Arsenate.*—The filtrate from (1) contains the arsenate which may be separated by acidifying with acetic acid and adding uranyl acetate in slight excess. The arsenate is precipitated as uranyl hydrogen arsenate, $UO_2HAsO_4$. If the precipitate should be colloidal or finely divided it may be collected and readily filtered by shaking with a pinch of asbestos fibre. The uranyl arsenate is readily soluble in hydrochloric acid from which it may be precipitated as sulphide by means of hydrogen sulphide.

The method has been successfully used by the author's classes in qualitative analysis as a means of detecting arsenate and arsenite either alone or in the presence of each other.

*Summary.*

A procedure is described for the separation and detection of arsenate and arsenite.

The separation is based on the relative solubility of their silver salts in sodium hydroxide.

Data in support of the procedure are furnished. The method is capable of detecting 1 mg. of either ion in the presence of 450 mg. of the other.—*Journal of the American Chemical Society*, March, 1921.

## THE PRESENT POSITION OF CHEMISTRY AND CHEMISTS.*

By Prof. N. T. M. WILSMORE.

(Concluded from p. 223).

In view of their peculiar notions of honour and humanity, it is not surprising that early in the war the Germans yielded to the temptation to make use of the great superiority in chemical resources which they then possessed, in an attempt to overwhelm the resistance of the Allies by launching surprise attacks with poison gas. As already mentioned, the end, from their point of view, very nearly justified the means; but it may be doubted whether towards the close of the war, when the Allies' reply in kind was becoming effective, they were quite so pleased with their innovation.

Owing to the ease with which free chlorine can be absorbed and rendered harmless, it was soon superseded for offensive purposes by various poisonous compounds, most of which, however, contained chlorine as a constituent. Of these compounds, perhaps the most important were phosgene and $\alpha\alpha'$dichlordiethyl sulphide, the so-called "mustard gas," the latter being first used by the Germans in July, 1917. Owing, apparently, to faulty organisation, on the part of the Department originally concerned, the production of poisons in Britain failed for some considerable time to meet requirements; but in April of 1918, the whole of the manufacture and supply was transferred to the Explosives Department. As this manufacture was given the highest priority, the whole of the comprehensive scientific and technical resources of the latter Department were at once applied to it, and a vigorous programme was taken up. In the meantime, a simplified method for making mustard gas by the action of ethylene on sulphur monochloride had been discovered in the Chemical Department of the University of Cambridge; and, although the working out of this method on a technical scale was still far from complete, its advantages over the cumbrous method used by the Germans were so obvious that it was decided to adopt it. An existing factory, which had been shut down, was rapidly reconstructed for the new manufacture, first on an experimental, and later on a large scale; and, owing to the strenuous and self-sacrificing labours of the technical staff, the process made such headway that by the following September 50 tons of this fearsome compound had been delivered to the shell-filling factories. This amount, however, was only a preliminary sample of what the factory was planned to make, but before it could get into its stride the war had ended.

It is of interest to note that the first consignment of shells filled with British mustard gas was delivered to the Australian Army Corps, and was used by it in the operation of finally piercing the Hindenburg Line at Bellicourt To quote General Monash, "Australian Victories in France," p. 255: "The first phase of the bombardment was of a novel character. For over two years the enemy had been using a shell containing an irritant and poisonous gas known as "mustard gas." . . . For a long time we had been promised that the British Artillery Service would shortly be supplied with a gas shell of similar character. It was moreover anticipated that the German gas mask would prove no adequate protection against this kind of gas. At last the new shell was forthcoming, and the first shipment from England, amounting to some 50,000 rounds, was placed at the disposal of the Australian Corps. My artillery action, therefore, opened with a concentrated gas bombardment of 12 hours, attacking probable living quarters, occupied defences, and all known or suspected approaches to them."

Later information from prisoners and other sources disclosed that the effect of this bombardment on the Germans had been most demoralising. For months previously the German troops had been assured that mustard gas would win the war for them; that no troops could stand against it; and that the British could not hope to make it. The subsequent disillusionment was, therefore, one more convincing proof that the game was up.

As the multifarious activities of the Explosives Department and of the other Departments under the Ministry of Munitions developed, the amount of research work which became necessary was very great. The Explosives Department itself had a laboratory specially set apart for research, and researches were also constantly in progress on the plant and in the laboratories in all the factories controlled by it. These resources, however, even when supplemented by those of the Research Department at Woolwich, proved inadequate to supply the mass of information which was constantly required; so a special Section of the Explosives Department was formed and entrusted with the duty of arranging for and co-ordinating research work in the laboratories of the Universities and technical schools throughout the country. Although greatly hampered by want of assistance, the teaching staffs of these various institutions responded enthusiastically to the call; so that innumerable problems involving chemistry, physics, engineering, and in fact every branch of science, were rapidly solved as they arose, and thus the

* Presidential Address, delivered before Section B (Chemistry), of the Australasian Association for the advancement of Science at the Meeting held in Melbourne.

smooth working of this gigantic war machine was made possible.

In this way the Department of Explosives Supply accumulated an immense and varied amount of most valuable information; and it was Mr. Quinan's earnest wish that, when the war was won, this information should be made available for the benefit of the industries, and especially the chemical industries of Britain and her Allies Fortunately this is now being done, the necessary editing having been placed in the able hands of Mr. William Macnab, who was himself one of Mr. Quinan's foremost colleagues on the Head-quarters Staff of the Department. The first instalment of the Reports, entitled "Preliminary Studies for H.M. Factory Gretna, and Study for an Installation of Phosgene Manufacture," has already been published. The latter portion of this Report contains a detailed discussion of the lay out of a plant to produce about 250 tons of phosgene per week, and affords an excellent example of Mr. Quinan's creative methods for attacking a new problem. The plant in question was in course of erection at the close of the war, and would have proved a valuable asset, had there been any further campaign. These Reports will be of the greatest value both to designers of chemical plant and to students of chemistry and chemical engineering, and should be added to the library of every university and technical school.

It should be mentioned that the Department of Explosives Supply also derived most useful help from the disclosure by private firms of information on various matters, which before the war had been jealously guarded as "trade secrets." This pooling of information already in existence in itself enabled great advances to be made. British chemical industry has been heavily handicapped in the past by the exclusiveness and secrecy of individual firms, whilst, on the other hand, its rivals in Germany and in the United States have derived great benefit from the exchange of knowledge amongst themselves. The commanding position of the British engineering trades has no doubt been largely due to the fact that in their case this policy of secrecy has for the most part been impossible, so that a discovery or invention made by one firm is at once of advantage to all.

My reason for dwelling so long on the work of British chemists in the war is two-fold. In the first place, the record of that work affords what should be convincing proof that chemistry and chemists are indispensable factors in the constructive work of peace. In the second place, the term "British" in this connexion includes "Australian," for Australian chemists formed no inconsiderable proportion of the technical staff of the Department of Explosives Supply. One cause of this was the supineness of the British Government early in the war, in allowing the chemists of the United Kingdom, who were all too few in any case for the chemical work ahead, freely to enlist in the fighting forces; so that, when the great factories were approaching completion, an urgent call for chemists had to be sent out to all parts of the Empire.

The future status of chemistry and chemists is intimately bound up with the quantity and quality of the training which chemists undergo. Hitherto many chemists have been using their generic name in an inexcusably loose fashion to include, not only thoroughly trained and competent all-round men, but also mere testers or works foremen, who have served a sort of apprenticeship in a chemical laboratory or works, but who, although they may sometimes be highly skilled in some one restricted branch of chemistry, have only the merest smattering of chemistry as a whole. The advancement of chemistry as a profession is seriously endangered by such a practice as this. We must begin by taking ourselves and our profession seriously, if we wish to be taken seriously by the members of other professions, and admitted by them to equal professional status.

On the whole, the general university curriculum for a science degree in chemistry has come out well from the test of the past few years. A broad and thorough training in pure inorganic, organic, and physical chemistry, together with a good working knowledge of mathematics, physics, and modern languages (including English), has shown itself to be the only satisfactory basis for any chemical career worth having. For teaching and for research in pure chemistry, a training on these lines would appear to suffice But the number of chemists who are disposed to, or are fitted for, these fields of work will always be limited, and the majority will have to seek their living as analysts or consultants or in the industrial field. For industrial chemists in general, some knowledge of engineering is a great advantage, as even when they do not themselves undertake the design and erection of plant, it enables them to discuss with engineers problems which are common to both in language which the engineer understands. For those who intend to specialise as engineer-chemists or chemical engineers, a training in engineering as well as in chemistry is, of course, essential. In this connection a perusal of the Report of the Discussion on "The Training and Work of the Chemical Engineer," held by the Faraday Society in London nearly four years ago, may be recommended.

The concensus of competent opinion in Britain at the present time is that a chemist, to be worthy of the name, should have had a systematic day training in all important branches of chemistry, extending over at least four years, and leading to a B.Sc. degree with first or second class honours in chemistry at the end of it. This qualification is now accepted as a minimum for admission to the Associateship of the Institute of Chemistry of Great Britain and Ireland. That Institute will, however, admit candidates for the Associateship who have obtained their training in evening classes, provided that this training has extended over at least five years, and that during that time they have been engaged in chemical work in the day time. In the United States a high standard of training for chemists is also required. A Committee of the American Chemical Society recently reported that the training of a professional chemist should extend over not less than five years, the final year being devoted chiefly to training in research. This last is a very important provision, because success in industrial as in academic chemistry depends on ability to attack new problems and to strike out into new lines of thought. There has been too great a tendency on the part of British-trained chemists in the past to go straight into works or into an analytical laboratory on the completion of their routine course, without wait-

ing to acquire any experience in research work at all. It is perhaps not unconnected with the high standard of training required that chemists in America are now commanding higher salaries than engineers of equivalent status.

It is to be hoped that the Australian Institute of Science and Industry, for which, as for so many advances in Australian science we are indebted largely to the initiative and energy of Prof. Orme Masson, may fulfil the purpose for which it was originally planned. For in that case it would open up wide fields of employment for Australian scientists in general and chemists in particular. Just now, however, there seems to be grave danger of the usefulness of the Institute being seriously hampered by a mixture of political interference and political inertia. In other words, it will probably ere long be dragged down into the dull and spiritless routine of a Sub-Department of the Commonwealth Public Service. The free spirit of scientific enquiry does not thrive in the atmosphere which surrounds the vote-catching machine. In any case, at the present intellectual level of our Australian Democracy, science could hope to catch but few votes. The prospects of the Institute maintaining the high level of achievement which it has hitherto shown, and becoming of permanent service to the country, like the British National Physical Laboratory, or the United States Bureau of Standards, are therefore growing dim. Already the country is the poorer through failure of the powers that be to take seriously and to give effect to recommendations which the Institute, or rather the Advisory Council has made. To cite one example—the question of supplies of liquid fuel in Australia is becoming desperate. Yet, instead of following up the valuable suggestion of the Advisory Council to utilise for the manufacture of industrial alcohol the immense amount of fermentable material now going to waste, it is proposed to spend untold sums in the less constructive but more showy and speculative enterprise of scratching the country for oil, which, in the opinion of many geologists, is probably not there. Unless the Institute of Science and Industry is given an autonomous position under scientific and technical control and free from the strangle-hold of official red tape, any money spent on it might as well be thrown away.

I must claim your indulgence for having dealt so long on matters connected with applied chemistry to the exclusion of pure chemistry. My only excuse is that the achievements of applied chemistry, especially those connected with the war, seemed likely to appeal more strongly to a general audience. In reality, however, as every chemist knows, the achievements of applied chemistry are merely the outcome of the more fundamental discoveries of pure chemistry, the ultimate source of all real advance in applied, as in pure chemistry, being the pursuit of chemical discovery for its own sake. That a realisation of this is growing in some technical circles is evident from the valuable papers on pure science, emanating from time to time from research laboratories belonging to manufacturing firms, of which the General Electric Co. of America is a notable example.

A first essential for real advance in technical chemistry in Australia is therefore adequate endowment and equipment for research as well as for teaching of our various university chemical departments Much in this direction has already been done, and the splendid record of the chemical schools of the older Australian universities and of the men whom they have trained shows that it has been money well spent. But much more must be done if we are to hold our own in the strenuous times ahead of us and contribute our proper share to the progress of our science. Hence it is sincerely to be hoped that the appeals for increased help to meet their ever-growing needs, which are being made by the various Australian Universities, will meet with a sufficiently generous response to justify Australia's claim to be a progressive and intelligent nation.

The progress in pure chemistry during the past few years has probably been as epoch-making as that of any previous period. We seem to be getting appreciably nearer to the heart of things. As has so often been the case, the most striking results have followed from the co-operation of chemistry with other branches of science, and above all with physics. To attempt to give even the most cursory summary of recent discoveries in the time now available would be fruitless. Art is long, and your patience must be growing short. Fortunately as regards one of the most important and fundamental problems of chemistry or physics, namely, the structure of the atom, the present position is to be laid before you by abler exponents.

I am afraid that the foregoing remarks have been somewhat discursive and fragmentary. Many of them have been made before by others, some of them many times. However, I have not attempted to say anything original, and certainly I have not succeeded. But if I have managed to supply my fellow chemists with a few reasons in a handy form for the faith which is in them, I shall be content.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

*Ordinary Meeting, May 5, 1921.*

PROF. C. S. SHERRINGTON, President, in the Chair.

THE CROONIAN LECTURE was delivered by DR. HENRY HEAD, F.R.S., on *"Release of Function in the Nervous System."* The following is a summary:—

Hughlings Jackson's law that destuctive lesions do not cause positive effects, but induce a negative condition, which permits positive symptoms to appear. Control of higher over lower centres. Structural lesions may remove this dominance, and so reveal the activity of subordinate centres; this is "disintegration" of function. Should the stimulus become abnormally intense, or central resistance be weakened, forms of reaction may break through which are normally suppressed; this is "escape from control."

§ 1. *Disintegration.*—Sherrington's experimental proof of Jackson's law. Decerebrate rigidity. Condition of the lower end of the spinal chord in man after division or abolition of conduction. The "Mass-Reflex." Wide receptive field, massive

reaction, facilitation of bladder and rectum. Thalamic over-reaction to potentially affective stimuli, both painful and pleasurable.

Vivid response after division of peripheral nerves; not "hyperæsthesia," for threshold may be high. Due to uncontrolled reaction of the spot system. Characteristics of protopathic sensibility; extent of stimulus of greater importance than its intensity; a warning mechanism; sensation diffuse and referred to remote parts. Excessive reaction both to pleasure and pain. Confined to parts which respond to pricking, heat, and cold, but not to lighter contracts.

§ 2. *Escape from Control.*—Integration of afferent impulses and of reflex activities in the central nervous system. Many afferent impulses never reach consciousness, but carry out co-ordination, &c., on reflex levels. Simplest sensory act, the product of prolonged integration and of a struggle for physiological dominance. Many impulses capable of arousing sensation are not permitted to reach the highest centres.

Visceral insensibility is a phenomenon of synaptic resistance rather than of absence of afferent impulses. Double supply of viscera (1) deep sensibility, responding to movement and pressure, but not to pricking, heat and cold; pain produced by excessive pressure or abnormal movement. (2) Protopathic, responding to pain, and in some organs, such as bladder and œsophagus, to heat and cold.

Referred pain. Spreads widely owing to intensity of stimulus, its duration, or to lowered central resistance (menstruation, fever, anæmia, psychical states). Similar escape from control of impulses from other sense organs which have been dominated in the acquisition of some new aptitude. Rotatory stimuli: adaptation and breakdown of control in central nervous system during aviation.

## ROYAL SOCIETY CONVERSAZIONE.

THE Conversazione was held at Burlington House, May 11, 1921, with the usual success, and a large number of exhibits were shown. A few that are likely to be of interest to our readers are noted below. An interesting lecture was given by the Rev. JOHN ROSCOE on the "*Primitive Races in Uganda.*"

Gravity Torsion Balance.

This instrument was designed by Baron R. Eötvös, Professor of Physics at the University of Budapest, in order to determine the variation of gravity over comparatively short distances, and to make experimental investigations on the form of the earth. The instrument has also been used in Hungary for the location of mineral deposits when the density of the mineral differed considerably from that of the surrounding strata.

Prof. ONNES, For.Mem.R.S., Sir R. A. HADFIELD, F.R.S., and Dr. H. R. WOLTJER. Apparatus and Specimens used in Research on the Influence of Low Temperatures on the Magnetic Properties of Alloys of Iron with Nickel and Manganese.

A series of iron-manganese and iron-nickel alloys were exposed to the temperatures of liquid air, liquid hydrogen, and liquid helium respectively, and the specific magnetism tested after return to atmospheric temperatures. Tests were also made during immersion in liquid hydrogen (—253° C.). The alloys with the higher percentages of manganese cannot be made magnetic even by immersion in liquid helium (—269° C.) The existence of one magnetic and one non-magnetic manganese-iron compound is shown to be probable

THE HON. SIR CHARLES PARSONS, F.R.S., and Mr STANLEY S. COOK. An attempt to reach high instantaneous pressure by the collapse of a hollow sphere of lead under external pressure suddenly applied by explosive.

The sphere is made up of two hemispheres placed together with tissue paper between and soldered around the periphery of the joint. In the cavity is placed the substance to be compressed. If its final diameter in nuclear form is 1÷200th that of the initial hollow and the pressure of the explosive 20 tons per square inch, the nuclear pressure produced is one million tons. The explosive is fired in six places simultaneously.

Mr. J. E. BARNARD. The Microscopic Appearance of Animal Tissues in Ultra-Violet Light.

Certain animal tissues show marked differentiation of structure when illuminated by means of ultra-violet light. The image obtained is a fluorescent one and the resulting colours or tints depend on differences of chemical constitution. Such images are often dissimilar from those resulting from staining reactions. The light filter used is glass transparent to ultra-violet radiations, approximately 300 to 400 $\mu\mu$ wave length, made by Messrs. Chance Brothers. This is combined with a quartz cell filled with a 20 per cent solution copper sulphate. The optical illuminating system is of quartz and the substage quartz condenser is of the "dark-ground" type. Apart from the biological interest of the method the image so formed is of considerable value for testing the optical qualities of microscopic objectives as the object so illuminated is a perfectly self-luminous one.

Radiological Branch, Research Department, Royal Arsenal, Woolwich. Pinhole photographs of the Coolidge Radiator Tube and Photographs Illustrating Protection in the X-ray Examination of Materials.

(1) Pinhole photographs illustrating the change in shape of the focal spot with current change. (2) Photographs illustrating the various parts of the target of the above tube which emit X-rays under varying conditions. (3) Photographs illustrating X-ray protection when radiographing large metal objects. (4) Photographs illustrating portable set designed and made in the Research Department, Woolwich, with complete protection for visual examination of materials.

Dr. E. E. FOURNIER D'ALBE. Latest Form of the Optophone.

The optophone is an instrument which enables totally blind people to read ordinary printed books and newspapers. It is based upon the reflection of beams of rapidly intermittent light from the type on to a selenium preparation, which produces sounds in a telephone varying according to the shapes of the letters. The instrument shown is kindly lent by the National Institute for the Blind, London, where it is in daily use.

## PHYSICAL SOCIETY.

*March* 22, 1921.

Prof. W. Eccles, F.R.S., Vice-President, in the Chair.

The following papers were read:—

"*The Effect of Viscosity on Orifice Flows.*" By Mr. W. N. Bond.

Determinations were made of the coefficient of discharge through an orifice 0·1469 cm. in diameter of solutions of glycerin and water, varying in kinematic viscosity from 0·01 to 7. The results are plotted in a manner which combines both purely turbulent flows in one graph. It is shown that the effect of slight viscosity is to increase the coefficient of discharge.

Discussion.

Mr. A. S. E. Ackermann said he had made experiments of a similar character in which the substance tested was clay. The clay was packed in a box with an orifice of from 3 to 20 mm. diameter in the bottom. The space above the clay contained air, and the pressure was raised by means of a pump.

The speaker then drew curves on the board to show his main results. With any particular orifice a certain initial pressure is required before any clay is forced out. As the pressure increases the rate of the flow becomes more rapid, and finally becomes very rapid indeed. The initial pressures and the orifice diameters were connected by the law $pd^{6.835}=5408$ for a clay with 29 per cent water. Similar results are obtained in forcing a disc through clay. The speaker mentioned that these and other results were given in a paper by him to the Society of Engineers, which was at present in the press.

Mr. Bond said the phenomena described by Mr. Ackermann were probably due to plasticity, rather than viscosity.

"*Viscosity of Water and Low Rates of Shear.*" By A. Griffiths, D.Sc., and Constance H Griffiths, M.Sc.

This paper describes the determination of the coefficient of viscosity of water by a method in which water is forced along glass capillary tubes of 1·5 to 2·0 mm. bore at rates of flow varying from 1 litre in two years to 1 litre in 24 years. The liquid fills a closed tubular circuit which for purposes of description may be said to be rectangular in shape. Two of the tubes of the rectangle are horizontal, and two vertical. The circulation is caused by a difference of density between the contents of the two vertical tubes. The difference is obtained by having a weak solution of uranine in one vertical tube, and pure water in the other.

In Apparatus I. the two vertical tubes are at a distance apart, and an allowance has to be made for the difference of temperature. In Apparatus II. a modification of the rectangular circuit is employed, the vertical tubes are close together, and no such correction is necessary. "Applying the temperature correction to the results recorded in this paper, the value of the co-efficient of viscosity at 18° is 0·010624 ± 0·000229 (assuming observations of equal weight), and 0·010569 gm./cm. sec. from Hosking's formula. Thus there is no experimental evidence that at the extremely low rates of shear (0·0017 to 0·0233 radians/sec.) the viscosity of air-free water in glass capillary tubes differs from its value at normal rates of shear (5000 to 10,000 radians/sec.)."

Discussion.

Dr. Vincent said it would be useful if the same apparatus could actually be used for high and low rates of shear. It would then be possible to find out any minor differences that existed better than by comparing results with different apparatus.

Dr. Rankine suggested that there was not much point in giving the results to so many figures. With regard to Dr. Vincent's suggestion it would probably be sufficient if the same capillaries were employed in conjunction with different driving apparatus for the different rates of flow, since it was in the capillaries that any errors were likely to arise. He thought, however, that the evidence of the paper was sufficient to show that there is no difference in excess of 1 or 2 per cent. This result may, of course, only hold for water.

Mr. W. N. Bond said that for viscosities as high as those used by Davidson and Kurt Molin, the viscosity changed by 50 to 100 per cent at low rates of shear.

Dr. W. Eccles said that the authors were to be congratulated on having surmounted very considerable experimental difficulties, particularly those due to temperature variations. Mr. Bond's remark suggests that with more viscous substances the range of variable viscosity is reached earlier, and this suggests that the author's next experiments should be with oils.

Dr. Griffiths, in reply to Dr. Vincent, said that in their experiments of eight years ago, in which they had been dealing with low rates of shear, though not so low as in the present experiments, they had for comparison made measurements in which the water was driven through the apparatus at ordinary rates. The difference in viscosity was less than one-third per cent in that case. With the present apparatus there would be no difficulty in geting rates of flow a hundred times greater than those dealt with in the paper.

"*A Method of Measuring Frequencies.*" By B. S. Smith and G. F. Partridge.

An heterodyne method of measuring frequency by comparison with a calibrated valve oscillator is described. The calibration is performed by means of two valve oscillators capable of giving frequencies of, say, 1000/sec. upwards. The frequency of the oscillations is raised alternately to give a beat note whose pitch is determined by comparison with a fork. Intermediate frequencies are found by interpolation on the calibration curve and a method of checking the capacities of the oscillator condensers is described.

For the measurement of acoustic frequencies the sounds are converted into alternating currents by means of a suitable transmitter.

Discussion.

Dr. Vincent said he would like the authors to give more detail about the coupling of the middle portion of the apparatus with the end parts. The authors appeared to have reached the same conclusion as himself that a triple arrangement was most suitable for measuring frequency differences. Dr. Eccles and he had called attention to a some-

what similar apparatus which they had termed a differential wavemeter. The two outer parts generated the oscillation and the middle part resonates sufficiently to either of them that you could do anything you liked to the middle circuit without affecting the capacity, &c. With the old arrangements it was necessary for the observer to stand in a particular position and to abstain from making any movement whatever. He had only one point of criticism. He thought it was desirable to get the electricity wholesale. A different supply should be used for the two circuits. It was important to use large batteries which could be left on for some time to give steady conditions. With such precautions he thought it would be possible to get an accuracy of 3 or 4 in 10 million.

Dr. D. Owen asked to what purposes the authors had actually applied their method. Could it be used for calibrating a Galton whistle; would the sounds in this case be sufficiently intense for the method to be applicable? He presumed the authors had determined by it the limit of audibility. This was usually stated to be 40,000 vibrations per second, but he had found people who were deaf above 10,000. Could the method be used to study the overtones of a valve set?

Prof. Rankine asked if the authors could actually let us hear a note of 10,000 frequency.

Prof. Eccles said there was often some diffidence in confessing to deafness to high notes as the limit of audibility was a function of age.

Dr. Rayner said he presumed the work had been done before the Abraham Block multivibrator was described.

Mr. Partridge, in reply to the discussion, said he had seen Dr. Vincent's work, but thought he was principally concerned with the measurement of inductances. As regards coupling, the middle circuit contained the telephone and crystal rectifier in series with two small secondary coils associated with the inductances of the outer circuits; there was no tuning. As regards the electric supply, their reason for using the 220-volt lighting circuit was because of its convenience on board ship. In reply to Dr. Owen, they had found the method very useful in determining the frequency of heavily damped steel diaphragms. It would be possible to use it with a Galton whistle if some means of picking up the sound at such high frequencies was available. In reply to Dr. Rayner, he was unaware of the device he had referred to.

(Mr. Partridge then demonstrated the production of a note of 10,000 frequency. This appeared quite loud to many of the audience, but was inaudible to others).

## SOCIETY OF PUBLIC ANALYSTS.

*Ordinary Meeting, May 4, 1921.*

Mr. Alfred Smetham, President, in the Chair.

Certificates were read for the first time in favour of Mr. W. N. Stokoe, B.Sc., A.I.C., and J. F. F. Rowland. Certificates were read for the second time in favour of Messrs. William Ellard Woolcott, and Thomas Henry Pope, B.Sc., F.I.C.

The following were elected Members of the Society: Messrs. Percy Nicholas Mould, and Walter Joseph Wright, F.I.C.

The following papers were read:—

"*Detection and Estimation of Illipé Nut Fat Used as a Substitute for Cocoa Butter.*" By Francis C. H. Tate and John W. Pooley, B.Sc., A.I.C.

Attention is drawn to the close similarity of the various physical constants of cocoa butter and illipé nut fat, and the consequent difficulty of detection and estimation. A method is suggested involving the combination into one factor of the following constants. Densities at 60°/15·5° C. and 99°/15·5° C.; melting points in °C. of the fat and fatty acids; viscosity at 60°C.; iodine value. The combined factor is obtained by multiplying together the factors in which the average constant for cocoa butter is lower than that for illipé nut fat, the product being multiplied by the reciprocal of the only constant in which cocoa butter is the higher, *i.e.*, the iodine value. From the average multiple factors thus obtained for the two fats the composition of any mixture is calculated. For approximate estimation when only small quantities are available, a method is suggested involving the use of the melting points of the fat and the fatty acids and the iodine value.

"*Notes and Demonstration on Apparatus for Determining Hydrogen Ion Concentration.*" By G. W. Monier Williams, O.B.E., M.C., M.A., F.I.C.

The determination of hydrogen ion concentration or absolute acidity, by the potentiometer method has not come into general use in analytical laboratories, chiefly owing to the cost of the electrical measuring instruments which are usually considered necessary. For work of the highest accuracy such apparatus is indispensable, but it is possible, for a very moderate outlay, to obtain results comparable in point of accuracy with ordinary titration methods. An apparatus of this nature was demonstrated, and the theory of the method and its application to analytical work discussed.

"*A Note on the Oil of Oats.*" By Ernest Paul, B.Sc., A.I.C.

The author examined the petroleum ether extract obtained by extraction of whole ground oats of the variety "Black Tartary." The extract was found to contain some lecithins, and analytical constants are given for the separated oil.

"*Estimation of Potassium in Presence of Sodium, Magnesium, Sulphates, and Phosphates.*" By H. Atkinson, B.A., A.I.C.

The method depends upon the relative solubility of these salts and the perchlorates of the metals in methyl alcohol. Potassium perchlorate has a low solubility in the liquid, while the perchlorates, sulphates, and phosphates of magnesium and sodium have a sufficiently high solubility to make the separation possible. Details of procedure are given and results of various tests.

## INSTITUTE OF METALS.

May Lecture on "*The Casting of Metals.*" By Prof. Thomas Turner, M.Sc., A.R.S.M.

In dealing with the subject of "The Casting of Metals," on the occasion of the Eleventh Annual

May Lecture of the Institute of Metals, on May 4, 1921, Prof. Turner stated that all metals have to be melted and cast before they are used, and that the casting of metals dated back to early antiquity. Every great nation has produced statuary in bronze; and there is no reason to believe that the quality of the older material cannot be equalled to-day, while the output has been enormously increased, and the percentage of "wasters" reduced. Among the physical properties which allow metals to be cast is viscosity, which is very low at temperatures just above the melting point, and thus metals can be poured as freely as water. Surface tension in metals is high, and this prevents them from wetting and adhering to the mould. The high co-efficient of expansion of aluminium introduces a special difficulty, and leads to fracture during cooling unless proper precautions are taken. Gases in non-ferrous metals are not so important as with steel, and any metal or alloy which does not develop gas by reaction, or does not unduly segregate, can be cast in a satisfactory manner provided that a suitable temperature is employed, that the mould is properly designed and made, and that the metal is skimmed and poured in the right manner. Pure metals of single substances, as a general rule, possess the same density whether slowly or quickly cooled. Those alloys in which there is an interval between the liquidus and solidus solidify over a temperature range and often expand when slowly cooled, as for instance, when cast in sand. Extensometer tests by Prof. Turner and his students have shown the nature and extent of such expansions in a number of typical alloys. The results of such tests agree with the density determinations, but the extensometer has the advantage of showing not merely the net result, but the sequence and amount of each volume change. In practice, one of the chief causes of failure is pouring at too high or too low a temperature. Other causes include such troubles as imperfect or badly fixed cores, faults in moulding, cracks, mis-runs or run-outs, and breakage in handling. In foundry work generally, the losses from all causes probably reaches quite 10 per cent of the output. The scientific man may introduce new ideas or processes and explain and remove difficulties. But in the end metal-casting is an art, and depends upon the skill, attention, and experience of the craftsman, who has acquired a knowledge which he may not be able to express in words, but which it is his desire to be able to impress upon the product which is the outcome of his labour.

## OPTICAL SOCIETY.

At a meeting of the Optical Society held on April 14, Mr. F. Twyman, of Messrs. Adam Hilger, Ltd., read a paper on "*An Interferometer for Testing Camera Lenses.*"

The Camera Lens Interferometer is an application to camera lens testing of the principles of an earlier instrument described in the *Philosophical Magazine* ("Interferometers for the Experimental Study of Optical Systems from the Point of View of the Wave Theory," *Phil. Mag.*, January 1918, vol. xxxv.); but it differs from the lens interferometer there described in that the camera lenses can be tested for oblique pencils.

The instrument gives aberrations in the form of an interference picture (which can be photographed), which is a contour map of the aberrations of wave front expressed in wave lengths of light in comparison with the wave front of a perfect camera lens.

A paper on "*The Testing of Heliograph Mirrors and the Measurement of Mirrors of Long Focal Lengths,*" was read by Mr. W. Shackleton. The method of testing the general surface consists in observing the reflection from the mirror of a system of squares on the test board, the magnification given by the mirror being utilised to determine the curvature. The method of examination is applicable to the rapid measurement of mirrors of long focal length especially of those forms silvered on the back, cata-dioptric mirrors, where the usual methods of measurement, test planes, or spherometers are inapplicable. Defects of curvature and distortion, astigmatism, and striæ in the glass can be detected, and also defects of silvering and bad polishing.

# CORRESPONDENCE.

## GALLIUM.

*To the Editor of the Chemical News.*

Sir,—In their interesting paper on gallium (Chemical News, 1921, cxxii., 176), T. W. Richards and S. Boyer state that the hydrogen evolved during electrolysis of a solution of crude gallium indium alloy gave a mirror in the Berzelius-Marsh apparatus, and that this deposit on spectroscopic examination showed the germanium line at $\lambda=4033$ Å.U., and a line at nearly $\lambda=4058$, probably due to lead.

With regard to the line $\lambda=4033$, the authors seem to have overlooked the possibility that this line is due to gallium itself. The visible spectrum of gallium contains the following lines (Uhler and Browning, *Am. Jour. Sci.*, 1916, xlii., 389; Eder and Valenta, "Atlas Typischen Spektren"; Dennis and Bridgman, Chemical News, 1919, cxviii., 245 et seq.; Bates, *ibid.*, 1920, cxx., 278, 279, 280, 281): $\lambda=3020{\cdot}61$; $4033{\cdot}18$; $4172{\cdot}22$; $5353{\cdot}81$; $5359{\cdot}8$; $6396{\cdot}99$; $6413{\cdot}92$ Å.U. The line at $4033{\cdot}18$ is remarkably close to that observed by Richards and Boyer, the more so as its intensity is given as 10 (Bates, *loc. cit.*). The reason that these authors do not attribute this line to gallium is probably that they are unaware of the existence of a gallium hydride, which has been described by Matignon (*Chem. Zeit.*, 1900, xxiv., 1062; *Compt. Rend.*, 1900, cxxxi., 891; Corrigan, Chemical News, 1919, cxix., 274, 275; see also *ibid.*, 1900, lxxxii., 303). This compound may have been formed by the nascent hydrogen, followed by volatilisation, and possibly subsequent decomposition of the product.

A hydride of lead has been described by M. J. Bouffort (*Journ. Soc. Chim. Ind.*, 1909, xxviii., 1126; see Corrigan, Chemical News, 1919, cxix., 275).—I am, &c.,

E. Tomkinson.

6, Kitchener Street,
Barrow-in-Furness, May 4th, 1921.

## NOTES.

SYNTHETIC RESINS AND VARNISHES.—The Electrical Research Association is actively interested in furthering the manufacture and use of electrical insulating materials made from synthetic resins and varnishes, and having the well-known heat-resisting characteristics associated with some of these materials. Leading manufacturers and users of the raw materials and finished products are already co-operating.

THE election of the Rt. Hon. J. H. Whitley, M.P., as Speaker of the House of Commons has caused him to have to resign the Joint Presidency of the Industrial League and Council, which he has held for so long in conjunction with the Rt. Hon. G. H. Roberts, M.P. Members and supporters of the Industrial League and Council will be glad to know that Viscount Burnham, C.H., has graciously consented to become Joint President. Viscount Burnham has almost from the inception of the League and Council taken a keen and personal interest in its work.

CAMPHOR GROWING FOR QUEENSLAND.—A method of obviating the importation of camphor from Japan at high prices is suggested by Mr. E. H. F. Swain, Director of Forests in Queensland. He advises the conversion of some of the waste lands along the Queensland coast into mixed forests of kauri and camphor, capable of supplying the entire camphor requirements of the Commonwealth. The soil indicated is peculiarly suitable for both trees. The establishment of a forest products laboratory in Queensland is also advocated in order to ascertain the best methods of obtaining tannic acid from eucalyptus kinos, commercial saponins from cupanias, gum arabic from bauhinias, essential oils from citron-scented gums and citron-scented ti-trees, caoutchouc from alstonias, starch and vegetable wool from macrozamias, and resin from grass-trees, as well as power charcoal and alcohol and other derivatives of wood distillation from characteristic Queensland trees.

FINSBURY TECHNICAL COLLLEGE.—The Governing Body of the Finsbury Technical College announce that the entrance examination for the Session 1921-22 will be held on Tuesday, September 20 next. Applications for admission should be forwarded to the College not later than September 15, on forms to be obtained from the Registrar, Leonard Street, City Road, E.C. The programme of the College is under revision, and will be issued in due course.

A PRETENDED ALLOTROPIC FORM OF LEAD.—Some years ago, Heller noted that compact metallic lead, placed in contact with acid solutions of lead salts, undergoes a remarkable change after a certain time. At first it is invaded by cracks, and soon falls to powder. Heller concluded that an allotropic form of lead is produced in consequence of a phenomenon analogous to the well-known transformation of ordinary tin into grey tin. This was confirmed by Cohen and Helderman, who studied the phenomenon by aid of the dilatometer. There is no chemical reaction, according to them, and the allotropic form obtained is denser than ordinary lead. Mr. A. Thiel resumed this study and subjected the question to a profound critical examination, concluding that it is not a case of allotropy, but one of chemical action He noted that this action only appears when the solution contains nitrate of lead, and that a well-known chemical phenomenon then occurs; dissolution of metallic lead with formation of nitrite of lead. There is a more readily attached eutectic between the crystals of metallic lead which explains the formation of cracks and pulverisation of the metal. The arguments of Thiel appear very convincing and existence of an allotropic form of lead should then be rejected.—*Revue Générale des Sciences*, January 15, 1921.

GLYCOL AS A GLYCERIN SUBSTITUTE.—During the war, lactates (perglycerin, percaglycerin) and glycol were utilised in Germany as substitutes for glycerin. Glycol is prepared from acetylene. It has a great resemblance to glycerin; it is more volatile and less viscuous. Fusion point—17·4° C.; boiling point, 197°; density at 0° C., 1·125; index of refraction at 20° C., 1·4723. Solubility in water, alcohol, and ether is perfectly analogous to that of glycerin. The Denigès reaction (heating with bromine water, addition, after cooling, of condensed sulphuric acid and a 50 per cent gayacol solution, blue coloration, violet in heating), gives a positive result with glycerin and glycol, but the latter does not give the Neuberg-Mandel reaction (boiling with a slightly alkaline hypochlorite solution, addition of olein and hydrochloric acid, boiling to violet or green colouration). The two substances can also be distinguished by the index of refraction. When this constant is $< 1{\cdot}428$ it is surely glycol, and when $> 1{\cdot}464$ glycerin.—*Matières Grasses*, February 15, 1921.

## NOTES AND QUERIES.

A correspondent wishes to know of a process for recovering tin from tin scrap, and where plant for such purpose can be obtained.

## New Patents.

THIS List is specially compiled for the *Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, W.C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

12461—Amend, O. P.—Refining petroleum distillates. April 30th.

12347—Ashcroft, E A.—Precipitating precious metals from cyanide solutions. April 29th.

12157—Boorman, H. G. T.—Treatment of nitrates for fertilizers, etc. April 27th.

12146—Brightmore, J.—Fixation of atmospheric nitrogen. April 27th

12129—Burgess, L.—Process of reducing aluminium oxide. April 27th.

*Specification published this Week.*

162026—Elmore, F. E.—Treatment of argentiferous lead-zinc sulphide ores.

*Abstract Published this Week.*

*Alumina; Aluminium Chlorides*—Mr. S. E. Sieurin, S E of Hoganos, Sweden, has been granted a Patent No. 159086, in this country for an improved process of obtaining alumina by the calcination of crystals of aluminium chloride obtained by saturating a hydrochloric-acid solution of aluminous material with gaseous hydrochloric acid, the mother liquor is displaced from contact with the crystals by means of a concentrated solution of aluminium chloride, before they are removed from the saturation vessel. After the precipitation of the crystals, the aluminium chloride solution is passed from below into the vessel containing the crystals, which latter together with the aluminium-chloride solution, are withdrawn from the bottom and separated, for example, by means of centrifugal action. The hydrochloric acid is recovered from the displaced mother liquor by distilling with sulphuric acid and is used for precipitating the aluminium chloride, or is dissolved in water for the dissolution of fresh aluminous material The sulphuric acid is concentrated for re-use and may be periodically freed from iron sulphate which is present as impurity, by cooling.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

## MEETINGS FOR THE WEEK

*Tuesday, May 24.*

Royal Institution, 3. "Occultism—Its Origin and Development" by Edward Clodd.

*Wednesday, May 25.*

Royal Society of Arts, 4.30.
Society of Chemical Industry, 7. (At Nottingham).
Institution of Electrical Engineers, 6. (Wireless Section). Discussion on "Long Distance Wireless Transmission" opened by Mr. C. F Elwell.

*Thursday, May 26.*

Royal Institution, 3. "The Architecture and Art of Hampton Court Palace" by Ernest Law.
Institution of Electrical Engineers, 6.

*Friday, May 27.*

Royal Institution, 9. "Elasticity" by A. Mallock.
Royal Society of Arts, 4.30.
Physical Society, 5.

*Saturday, May 28.*

Royal Institution, 3. "Gnosticism and the Science of Religions" by F. Legge.

# NOTICES.

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THE CHEMICAL NEWS.

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# THE METALLIC HYDRIDES AND THE ACTION OF HYDROGEN ON THE METALS.

By E. TOMKINSON.

## PART I.—*The Metals of the Alkaline Earths.*

THE above phenomena have been aptly summarised by J. F. Corrigan in a recent paper CHEMICAL NEWS, 1919, cxix., 259, 273). It is the purpose of this paper to give an account of the hydrides of the alkaline earth metals, and to direct attention to certain of their applications.

Phenomena due to absorption of hydrogen, and in some cases) to formation of hydrides are of much more frequent occurrence than might at first thought be realised. Thus we have the crytallisation and sublimation of certain metals on heating in hydrogen, the absorption of gases (principally hydrogen) in X-ray, vacuum, and spectroscopic tubes; the anomalies experienced in the spectra of metals in a hydrogen atmosphere; certain reactions in iron and steel manufacture; the adsorption theory of catalysis, and hydrogen overvoltage.

These phenomena will be dealt with in subsequent papers, and in connection with the metals calcium, barium, and strontium, we may consider the absorption of gases having a practical application, viz., in Soddy's vacuum furnace Calcium, barium, and strontium, all combine with hydrogen on heating, forming solid hydrides of the general formula $RH_2$ (H. Moissan, *Bull. Soc. Chim.*, 1899, (3), xxi., 876; Guntz., *Compt. Rend.*, 1901, cxxxiii., 1209), in which the elements exhibit their normal valencies.

### *Calcium and Hydrogen.*

Metallic calcium, on heating, absorbs all gases except the inert monatomic gases. This property has been used in Soddy's vacuum furnace (F. Soddy, *Proc. Roy. Soc.*, 1907, lxxviii., A, 429; E. C. C. Baly, "Spectroscopy," 1918, pp. 433-435; W. W. Coblentz, *Bull. U.S. Bureau of Standards*, 1914, xi., 186-187; see also Sir W. Crookes, CHEMICAL NEWS, 1919, cxix., 47) in which heated calcium is used to separate all the gases which are chemically valent, leaving only the inert gases, whose spectra are easily recognisable. If the latter are absent, an almost perfect vacuum is obtained. In this operation it is important not to heat the calcium too strongly, as, if this is done, the calcium hydride, nitride, &c., formed at a lower temperature, will be dissociated. Coblentz (*loc. cit.*, p. 186) found that combination between calcium and nitrogen, hydrogen, &c., took place at above 300° C. This investigator also noticed that by the decomposition of the hydride formed, the calcium may be sublimed up the sides of the tube in which it is heated, which phenomenon is known to occur with metals whose hydrides have not been isolated (*e.g.*, nickel). The idea of the use of calcium as an evacuator was a result of the work of Moissan (*Compt. Rend.*, 1897, cxxvii., 29, 497, 584; 1898, cxxix., 1757), and of Arndt (*Ber.*, 1904, xxxvii., 4733). Moissan used calcium to absorb the nitrogen and traces of hydrogen which are always present if a mixture of lime and magnesium powder has been used in the preliminary treatment of air for the isolation of the rare gases, and he used this method in his estimation of the argon contained in the air (finding it to be 0·931-0·938 per cent—see *Compt. Rend.*, 1903).

*The Spectrum of Calcium in Hydrogen.*—As a result of an investigation of the arc spectrum of magnesium in hydrogen, Fowler concluded that the spectrum observed under these conditions is that of magnesium hydride. A similar investigation was undertaken for the case of calcium by Olmsted (*Astrophys. Jour.*, 1908, xxvii., 66), who found two main groups of bands extending from $\lambda = 6404$ Å.U. to $\lambda = 6367$ Å.U. This spectrum is probably due to calcium hydride. The subject has been recently investigated by King, (A. S. King, *Astrophys. Journ.*, June, 1916) who confirms Olmsted's view. It may be mentioned as a general rule, that compounds always give band spectra, which are emitted by molecules, whilst line spectra are emitted by atoms. (*Note.*—Some elements give band spectra with feeble excitation, but line spectra with a sufficiently intense discharge, as also do monatomic elements. The banded spectrum, due to calcium hydride is at a maximum between 1900° and 2200° C. The hydride would be almost completely dissociated at these temperatures (Gautier, *Compt. Rend.*, 1902, states that the alkaline earth metal hydrides are strongly dissociated at 600° C.), but it is as well to remember that (1) the hydrides may become stable at these temperatures; (2) the dissociation may be modified by the electrical conditions; and (3) a very small quantity of the hydride would give the spectrum in question. This question is also of interest in connection with the temperature of stars of the Antares type (Antarian bands), for the presence of the banded spectra of titanium oxide and magnesium and calcium hydrides in their spectra would go to show that their temperatures may be relatively low. On heating calcium in hydrogen, it takes fire and burns energetically, forming $CaH_2$ (Moissan).

It is of further interest to note that W. N. Hartley (*Proc. Roy. Soc.-Dublin*, 1907) found certain curious effects in the spectrum of calcium in hydrogen (without a jar in circuit), finding *bands* in the orange and red. He found that at pressures of less than 5 mm., no distinct spark occurred, but there were "bright stationary spots of white light on the negative electrode, which were less bright on the positive electrode, not in one spot, but all over it." Hartley concluded that the phenomena were connected with the discharge of electricity from hot calcium and from hot lime described by F. Horton (*Proc. Roy. Soc.*, 1907). It seems to me that all the observations were due to the spectrum of calcium hydride, for the spectra were banded, and the light emission at the electrodes may well have been due to combination between the calcium and hydrogen. The question will be again discussed when we consider platinum.

*The Technical Preparation of Calcium Hydride and its use for the Generation of Hydrogen for Aeronautical Purposes.*—The commercial product

is known as "hydrolith," and is of some technical importance, especially for the rapid generation of hydrogen, thus: $CaH_2+2H_2O=Ca(OH)_2+2H_2$, the amount of hydrogen evolved, of course, being double that combined as $CaH_2$. This method of generating hydrogen has, on account of its extreme rapidity, been adopted by the French army for the filling of dirigibles. Although its cost prohibits the widespread use of this method, yet, as pointed out by Fournois (A. Fournois, "La Fabrication de l'hydrogène pour le gonflement des Ballons," *Revue Générale des Sciences pures et Appliques*, June 15, 1915, xxvi., 339), the cheapness with which the material can be transported as compared with the cost of transport of cylinders of hydrogen more than compensates for its original cost. In 1915, according to Fournois, the total cost of an outfit for 50,000 cm. was only about one-third of that of hydrogen in cylinders; one vehicle sufficing for transporting the hydrolith plant, as against tyelve for gas cylinders. A vehicle carrying six generators gives an output of 500 cubic metres per hour. The cost of the material was then 5 francs per kgrm.,, but there appears to be no demand for the substance in this country at present; at least, I have not been able to procure any.

The method for the manufacture of calcium hydride for the above purpose was patented by G. F. Jaubert in 1902 (French Patent 327,878). The hydrogen required for this purpose is obtained as a bye-product in several operations; for example, in the electrolytic production of soda from brine, and it is very necessary that it be pure. Oxygen as an impurity may give rise to explosions and causes the formation of CaO. The presence of oxygen may be avoided initially by the introduction of pierced metallic or asbestos diaphragms between the electrodes. If the hydrogen is produced by electrolysis of water, the oxygen may be absorbed by a mass of liquid zinc amalgam (in this connection, see *Amer. Chem. Jour.*, 1897, xix., 810; "Industrial Chemistry," Martin, 1918, Inorganic I., pp 114-115; and Thorpe, "Dict. App. Chem.," 1913, iii., 60). The hydrogen in as nearly pure condition as practicable, is then passed over the calcium contained in an iron tube heated in an electric furnace.

In a later modification of this method, horizontal iron retorts filled with hydrogen are used in place of the above-mentioned iron tube (Jaubert, *Comptes Rendus*, 1906, cxlii., 788). Thus manufactured, the product contains 90 per cent $CaH_2$, and 1 kgrm., on treatment with water, yields a cubic metre of hydrogen, which is free from ammonia and acetylene (J. Prats-Aymerich, *Anal. Fis. Quim.*, 1907, v., 173). The 10 per cent impurity is chiefly lime and calcium nitride. According to Jaubert (*loc. cit.*), the $CaH_2$ was already in use in 1906 as a means of hydrogen generation for aeronautics.

*Laboratory Preparation of Calcium Hydride.*—Metallic calcium, contained in nickel boats, is placed in a glass tube having one end sealed and hydrogen at a pressure of 4-5 cm. of mercury is passed in, the tube and its contents being heated to redness; the temperature, however, being kept low enough to prohibit any combination between the calcium and the nickel (Thorpe, "Dict. App. Chem.," 1913, i., 599).

*Properties of Calcium Hydride.*—When prepared in a pure condition, calcium hydride forms a fused mass of slender transparent plates, of specific gravity=1·7, and stable in vacuo at 600°. On heating in air or oxygen, calcium hydride burns brilliantly—thus $CaH_2+O_2=CaO+H_2O$.

It is attacked by phosphorus, the halogens, and sulphur on heating (Moissan, *Comptes Rendus*, 1897, cxxvii., 29), and decomposes alcohol In most of its reactions, calcium hydride acts as a violent reducing agent, the exceptions being in some organic reactions, where condensation generally ensues.

Calcium hydride reduces many metallic oxides very easily (F. M. Perkin and L. Pratt, *Trans. Faraday Soc.*, 1907). Cupric oxide is especially easily reduced: $2CuO+CaH_2=CaO+2Cu+H_2O$, this occurring by the use of a match. Pyrolusite, tinstone, and hematite are readily reduced, but the mass must be heated in a furnace or the reaction started by means of a fuse. Zinc oxide is unreduced. Wolframite and rutile react with difficulty, whilst lead and antimony sulphides are readily reduced. Boron can be prepared from boric anhydride or from borax, and small quantities of silicon can be made from silica. It is to be noted that although wolframite is reduced with difficulty by calcium hydride, yet this is easily accomplished by metallic calcium.

Owing to the conflicting statements regarding certain reactions of calcium hydride, the subject has been recently re-examined by Reich and Serpek (*Helv. Chim. Acta*, 1920, iii., 138). A 13·2 per cent yield of formic acid is obtained by gently heating a mixture of calcium hydride with sodium carbonate or bicarbonate. According to these authors, only a small amount of ammonia is produced by the interaction of calcium hydride and nitrogen at 500°, the main reaction resulting in the formation of calcium nitride and hydrogen. Of course, the nitride could be decomposed by water (or steam), but this would certainly not be a commercial success, for then the calcium nitride could be made by the direct union of its elements, which however, is far too expensive.

$$3CaH_2+N_2=Ca_3N_2+3H_2$$
$$Ca_3N_2+6H_2O=2NH_3+3Ca(OH)_2$$

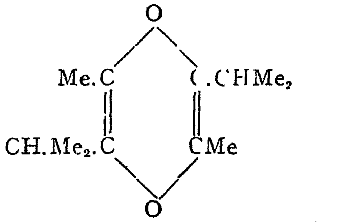
This result does not agree at all with that of Kayser French Patent, 350,966; see Chemical News, 1920, cxxi., 177), who states that the reactions are:—

$$\begin{cases} 3CaH_2+2N_2=Ca_3N_2+2NH_3 \\ Ca_3N_2+6H_2=3CaH_2+2NH_3 \end{cases}$$

in which the only material continuallly required is nitrogen. A further quantity of ammonia is available in the $Ca_3N_2$ (above). Moissan (*Compt. Rend.*, 1898, cxxvii., 29) stated that nitrogen had no effect on calcium hydride. It seems probable that a catalytical effect occurs, as is the case in the absorption of nitrogen by calcium carbide to give cyanamide Calcium hydride reduces carbonic oxide at a dull red heat with formation of methane, hydrogen, and formaldehyde (the latter with 16 per cent of CO).

*Organic Reactions of Calcium Hydride* (Reich and Serpek, *loc. cit.*).—Acetone reacts with cal-

cium hydride forming mesityl oxide (b.p. 128-130°) and



a substance of the annexed formula (b.p. 226°-231°).

With acetophenone, $C_6H_5.CO.CH_3$, at 240°, condensation products are formed. By reaction with quinoline, $C_9H_7N$, there is formed at 220°, β-, -*diquinolyl*, consisting of needles, m.p. 190°.

Pyridine, at 160-165°, yields a little of a crystalline substance which is not apparently identical with any known dipyridyl (m.p. 54-56°). No action occurs at various temperatures between calcium hydride and ethyl acetate, nitrobenzene, anthraquinone, and other compounds.

On adding calcium hydride to a solution of ferric chloride in ether, a brown precipitate is produced, of the composition $Ca_3FeCl_5(C_4H_{10}O)_3$, soluble in water to an acid solution. Reich and Serpek conclude that in organic reactions, calcium hydride acts as a reducing agent only at very high temperatures, and that its use for hydrogenaiton is very limited, especially as it generally leads to condensations.

It is probable that more satisfactory results would be obtained by the use of catalysts, such as are employed in modern processes for the hydrogenation of oils.

It was proposed by Ebler (*Zeit. angew. Chem.*, xxviii., 25) to utilise calcium hydride alone or in conjunction with calcium carbide, in reducing mixed barium-radium sulphates to the sulphides (the mixture containing $CaSO_4$, $PbSO_4$, $BaSO_4$, $FeSO_4$, and 0·35 mg. radium metal per kg.); the reactions being $MSO_4+4CaH_2=MS+4CaO+H_2$—(1) or $MSO_4+4CaC_2=4CaO+MS+8C$—(2), reaction (1) occuring spontaneously, giving a reduction of 75 per cent in the low-grade material and 80·5 per cent in the high grade.

With low-grade sulphate, three parts of calcium hydride and one of calcium carbide effected a 64 per cent reduction, whilst high-grade sulphate with one part hydride to two parts carbide gave a 60 per cent reduction. But although the reactions with calcium hydride and carbide are spontaneous the cost of the latter is prohibitive (see U.S. Bureau of Mines, *Bull.* 104, 1916, pp. 71-72).

The successful commercial utilisation of calcium hydride will depend in a great measure on the cost of the metal. The production of metallic calcium in quantity is a very difficult operation, and the present position is shown in a paper by P. H. Brace ("Some Notes on Calcium"—Paper read before the Institute of Metals," March, 1921; *Engineering*, March 11, 1921, vol. cxi.).

*Barium and Hydrogen.*

Barium and hydrogen combine readily on heating, with formation of barium hydride, $BaH_2$ Guntz, (*Compt. Rend.*, 1901), the existence of which was first investigated by Winkler. It is remarkably stable, and can be slowly sublimed in a current of hydrogen at 1400° without decomposition.

On heating barium hydride in a current of nitrogen at a high temperature, it is converted into barium nitride, $Ba_3N_2$ (Guntz). Barium hydride possesses the curious property of still further absorbing hydrogen, but no definite hydride higher than $BaH_2$ is formed (Henri Gautier, *Compt. Rend.*, 1902). This phenomenon probably occurs with palladium, copper, and other metals.

*Strontium and Hydrogen.*

*Strontium hydride*, $SrH_2$. This compound has been investigated by Guntz (*Compt. Rend.*, 1901, cxxxiii, 1209; cxxxiv., 838) and also by Gautier (*Compt. Rend.*, 1901, cxxxiv., 100, 1108). Its chemical behaviour generally resembles that of calcium hydride, and is decomposed by water in a similar manner. $SrH_2+2H_2O=Sr(OH)_2+2H_2$.

Strontium hydride is prepared by heating strontium (prepared by electrolysis of an aqueous solution of strontium chloride with a mercury cathode, and subsequently volatilising the mercury by cautious heating), strontium amalgam, an alloy of strontium with 50 per cent of copper, or one with 55 per cent of cadmium, to a dull red heat in hydrogen, which, in the case of the alloys, is slowly absorbed and the Cd or Cu volatilises. Towards the end of the operation, the temperature is raised until the mass fuses, which occurs at a red heat. On being more strongly heated, it decomposes, its dissociation pressure being 100 mm. at 1000° C.

Like barium hydride, strontium hydride can absorb more hydrogen.

In conclusion, I think that it has been shown that the hydrides described are well worthy of further investigation, which I hope to make in the near future.

6, Kitchener Street,
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15th April, 1921.

## A NEW METHOD FOR THE DETECTION AND ESTIMATION OF COBALT.

By S. A. BRALEY and F. B. HOBART.

IT was noted by one of us when testing for nickel with dimethylglyoxime a brown solution always resulted when cobalt was present in the solution. This study was undertaken to determine whether this was a specific property of cobalt that might be used as a definite qualitative test and possible colorimetric quantitative method for estimating small amounts of the element.

Böttger states that "cobalt salts give with dimethylglyoxime a brown-coloured compound" (Böttger, "Qualitative Analysis," 2nd Ed., p. 212). Treadwell-Hall and Mellor both state that when determining nickel with dimethylglyoxime not more than 0·1000 grm. of cobalt should be present in 100 cc. of solution, but give no explanation (Treadwell-Hall, "Analytical Chemistry," 3rd Ed., 1913, ii., 130; Mellor, "Treatise on Quantitative Inorganic Analysis," 1913, p. 394).

Tschugaev discusses complexes of cobalt and dimethylglyoxime with pyridine and ammonia (Tschugaev, *J. Chem. Soc.*, 1914, cv., 2187), and Matsui gives a test for cobalt using dimethylglyoxime and ammonium polysulphide (Matsui,

TABLE I.—*Showing Result of Adding $NaC_2H_3O_2$ or $NH_4OH$ and Dimethylglyoxime Solution to Some Metallic Solutions in Very Dilute Acid.*

| Metal. | Colour in $NaC_2H_3O_2$ or $NH_4OH$ solution. | On addition of dimethylglyoxime. |
|---|---|---|
| Nickel | No colour | Red precipitate |
| Iron, ferrous | Green solution or precipitate | Light red solution or precipitate |
| Ferric | Red solution or brown precipitate | Darkens giving red solution or precipiatte |
| Copper, cuprous | Blue to green solution or precipitate | Dark green to brown solution |
| Cupric | Dark green solution or precipitate | Brown solution or precipitate |
| Cobalt | No colour | Brown solution or precipitate |

*J. Tokyo Chem. Soc.*, 1918, xxxix., 459). In no case, however, is mention made that the brown colour of cobalt dimethylglyoxime solution might be used as a qualitative test.

### *Materials.*

Kahlbaum's cobalt and nickel carbonates ("nickel free" and "cobalt-free", respectively) were carefully tested for impurities and used for all tests.

### *Experimental.*

*Qualitative Considerations.*—It was first necessary to determine what metals give coloured solutions with dimethylglyoxime under the conditions of the nickel precipitation. The following table shows the results of the test in solutions containing about 0·05 mg. of the metal per cc.

If, however, mineral acid be added to any of the above solutions the colour of the metal in that particular acid prevails except in the case of cobalt in which the brown colouration remains, its intensity decreasing somewhat on the addition of the acid but depending principally upon the quantity of cobalt present. A solution containing 0·0005 mg. per cc. presents a very distinct colour. Considerable quantities of iron or copper, of course, mask the colour, but in the regular qualitative scheme these elements are removed and the filtrate resulting from the nickel confirmation gives the test directly, it being necessary only to acidify with mineral acid in order to exclude the possibility of the colour being due to slight contamination with the previously-mentioned elements.

*Quantitative Considerations.*—A Dubosq dipping colourimeter was used for all colourimetric comparisons.

The first procedure was to treat a solution of cobalt chloride according to the procedure for the determination of nickel with dimethylglyoxime as given in Treadwell-Hall (*loc. cit.*) with slight modification. On acidifying the resulting solution with hydrochloric acid it was found that the colour was not sufficiently constant for a quantitative comparison, although it works very well for a qualitative test. Acetic acid was then substituted for the hydrochloric acid, thus decreasing the hydrogen-ion concentration, when much better results were obtained. To reduce the hydrogen-ion concentration further sodium acetate was added to the slightly acid solution.

The actual method used was as follows. The cobalt, or cobalt and nickel, solution prepared as for the determination of nickel was slightly acidified and 10 per cent sodium acetate added until the solution was practically neutral, heated to boiling and dimethylglyoxime added in excess. (If nickel was present it was filtered off at this point.) The solution was then allowed to cool slowly and when cold comparisins were made between solutions of different strengths as standards. Because of the possible effect of excess of the dimethylglyoxime reagent or of sodium acetate these were alternately made the variable in several test solutions. Excess of sodium acetate had no effect on the accuracy while a large excess of the glyoxime reagent decreased the accuracy. This should make no difference in the determination, however, as the amount of dimethylglyoxime added in a nickel determination is based on the approximate total percentage of nickel and cobalt present, and hence a large excess of the reagent would never be present.

To show the accuracy of the results in an actual determination mixed solutions of nickel and cobalt were prepared and analysed in this way; the results are given in Table II.

TABLE II.

| Ni present | Ni found | Co present. | Dimethylglyoxime added (1% solution). Cc. | Co found. |
|---|---|---|---|---|
| 0·0468 | 0·04664 | 0·00862 | 30 | 0·00822 |
| 0·0468 | 0·04657 | 0·00862 | 30 | 0·00822 |
| 0·0468 | 0·04662 | 0·00431 | 30 | 0·00383 |

Solution and washings diluted to 100 cc.; comparisons made with cobalt solutions containing 0·00431 g. of Co and 5 cc. of dimethylglyoxime reagent in 100 cc.

Many other results on other concentrations of the salts gave data comparable with the above.

While the method gives very good results for small amounts of cobalt in the presence of much larger amounts of nickel some points should be kept in mind. The solution or filtrate should be allowed to cool slowly as the intensity of colour seems to vary slightly with the rate of cooling and in the sodium acetate solution copper and iron must of course be absent.

### *Summary.*

1 It has been found that dimethylglyoxime always gives a brown-coloured solution with cobalt which does not disappear upon the addition of mineral acids as does the colour of other metal glyoximes, and hence can be used as a sensitive qualitative test for cobalt, in the absence of such interfering substances as copper and iron.

2. In the absence of the elements which give coloured solutions or precipitates with sodium acetate or dimethylglyoxime (with the exception of nickel) the brown colour of cobalt dimethylglyoxime is proportional to the concentration, and hence can be used as a colourimetric method for this element, when the solution is prepared by use of acetic acid and sodium acetate.—*Journal of the American Chemical Society*, March, 1921.

## THE PREPARATION OF CATGUT.

By Major F J. W. PORTER, D.S.O., R.A.M.C.rtd., Bombay.

MANY years ago the preparation of catgut by means of iodine was hailed with satisfaction by the majority of surgeons, for it was undoubtedly a great improvement on the unsatisfactory methods then in use. It soon became obvious that the catgut prepared in this way becomes brittle after a time and it cannot be stored for long periods. For a good many years I have abandoned this method and the catgut prepared with biniodide of mercury has proved so satisfactory that I venture to bring it to the notice of those who may still be struggling with the iodine prepared material.

Very reliable catguts are now put up by various makers, but for hospitals or for surgeons who do a good deal of private practice, the cost is prohibitive.

I purchase Hartman's fat-free catgut in hanks which contain a dozen strands each about six feet in length. Each strand is coiled round the fingers into a small circle, which is held in position by winding a few turns of the end of the gut round the coil so as to keep it from becoming undone. I usually prepare about a dozen hanks at a time.

The coiled strands are put into a wide mouth bottle of about 10 oz. capacity, and into it is poured enough distilled water in which two soloids of biniodide have been dissolved, so as to completely cover the gut. The solution is about 1 in 250.

The catgut swells up, and the watery biniodide penetrates into the interior and kills any spores which may be lurking there. The importance of this is obvious when one knows of cases of tetanus which have undoubtedly occurred from germs set free from the interior of catgut after the outer layers have been absorbed.

Biniodide of mercury is one of the most powerful antiseptics we possess, as the following table will show:—

| | | | |
|---|---|---|---|
| | Thymol ... .. | 1 in | 83 |
| | Boric acid ... .. | 1 ,, | 140 |
| | Carbolic acid ... | 1 ,, | 333 |
| 40 per cent | Formaldehyde | 1 ,, | 10,000 |
| | Hydrogen peroxide | 1 ,, | 20,000 |
| | Mercuric chloride | 1 ,, | 14,300 |
| | Mercuric iodide | 1 ,, | 40,000 |

The gut is allowed to remain in this watery solution for three days.

The water is then poured off and about 3 or 4 oz. of methylated spirit added to the catgut which is well shaken up. This causes a certain amount of dehydration.

This spirit is then removed and the bottle filled with methylated spirit in which two more soloids have been dissolved.

The material is ready for use after seven days, and it may be stored in the solution for years without deterioration. I wind it on glass reels according to size, and knot each strand to the next. The reel is kept in a wide-mouth ligature bottle, from which it is cut off in the required lengths at operations.

The gut is impregnated with a powerful antiseptic which does not appear to irritate the tissues. It is hard, but very pliable, and any slight accidental infection by the fingers in the act of using it may confidently be expected to be dealt with by the large amount of antiseptic which exists on the surface of the gut.

The strength of No. 1 catgut prepared in this manner must be seen to be realised, and this size is quite strong enough for the ligature of any vessel which may be encountered in an ordinary incision in any part of the body. It is of course obvious that the finer the gut which can be used for this purpose, the better the result will be.

If a more lasting gut be desired, it may be prepared in the following manner. Take some coils of catgut prepared as described above, and put them in a wide-mouth bottle. Fill it with distilled water and shake for a few minutes so as to remove some of the spirit from the outer layer of the gut. Pour this off and add distilled water to which a little formalin has been added. Leave it soaking in this for two days or longer if more durable catgut is desired. At the end of this time pour off the formalin solution, dehydrate with a little spirit, and then fill the bottle with methylated spirit in which biniodide has been dissolved in the strength as before indicated. The gut may be kept in this solution indefinitely.

No. 3 catgut prepared in this way will last in the abdominal wall for about three weeks.—*Indian Medical Record,* February, 1921.

## FUEL ECONOMY AND NATIONAL PROSPERITY.

THE completion of 18 months' active existence of the Fuel Economy Committee of the Federation of British Industries, and of six months' practical work by the Technical Sub-Committee seem to offer a suitable occasion for some general report of progress and review of the outlook in the Fuel Economy Movement. For these reasons the Federation has published the present *Review*, with the co-operation of recognised authorities in the different branches. It is hoped that it will serve to bring home to those members of the Federation who have not already done so, the urgency of the need to give attention to the question of fuel efficiency each in his own works, and at the same time to emphasise the practical value of the service which the Fuel Economy Department places at their disposal.

The high cost of coal gives the fuel factor a greater importance in production policy than it has ever had before. Therein lies a danger that manufacturers may be forced into taking action without due consideration. It cannot be too strongly urged that a timely review of the whole situation and its possibilities should be made before deciding upon future programmes for securing the best results from the fuel consumed. It seems beyond dispute that henceforward no large works will be complete without a fuel control organisation as part of its regular equipment, while every industrial establishment great or small will find it necessary to instruct and encourage stokers in up-to-date firing practice, and call in expert advice on the most effective use of existing plant and test instruments.

In the pages of the *Review* an effort has been made to present the problem in a general way from the various points of view.

An account is given of the work of the Fuel Economy Department of the Federation of British Industries, describing the origin of the service,

the personnel of the Technical Sub-Committee, and the lines upon which investigation is carried out on behalf of those manufacturers who apply to the Federation for advice and help. Attached to this article is a summary of the Memorandum on Boiler Efficiency prepared by the Technical Sub-Committee, together with diagrams illustrating the losses of sensible heat in flue gases, and the principal sources of heat loss in boilers. A further article takes the form of a report on industrial fuel supplies and gives the result of the coal and coke *questionnaire* issued by the Federation of British Industries last year. The failure of a certain proportion of manufacturers receiving the *questionnaire* to co-operate by giving the particulars asked for is to be taken as a proof that much educational work still remains to be done before it can be said that British industry as a whole is alive to the importance of the fuel factor in successful production.

No name ranks higher in the scientific-industrial world than that of Sir Robert Hadfield. As the inventor of manganese steel and low-hysteresis steel, as an untiring investigator in many fields, and as the head of a great manufacturing organisation, he holds a position which may be described as unique, and his thoughtful and statesmanlike article, dealing with some leading aspects of the fuel economy movement, will not be without influence in helping to crystallise the thoughts of those who have not yet grasped the fact that the efficient use of fuel is now a vital factor in competitive manufacture.

Coming to the papers dealing specifically with the several sources of power, Mr. David Wilson brings a wide knowledge to bear on the fundamental question of coal economy as applied to steam raising. His work as technical adviser to the Coal Controller is too well known to call for comment or elaboration, and the advice which he gives, based on experience of different plants, examined during the war, when the need for economy was pressing for other reasons, cannot be neglected by the responsible heads of industry. Economy of the national coal resources by the generation of electricity of the production of gas are dealt with by Mr. J. S. Highfield and Sir Dugald Clerk, both men of the front rank in their respective spheres and needing no introduction to our readers. In his paper outlining the recent developments in the economical generation of power, Mr. P. R. Allen broadly surveys the coal resources of the world and gives use the benefit of his views on hydro-electric power and such interesting possibilities as the utilisation of the force of the waves and tides.

The thanks of all who are interested in the welfare of British industry are due to these gentlemen for their willing co-operation in making possible the publication of the *Federation of British Industries Fuel Economy Review*. Due acknowledgment must also be made to the *Iron and Coal Trades Review*, and to the Mines Department of the Board of Trade for the valuable assistance rendered by supplying statistics and information.

So far as we are aware, no publication has been issued before in this country devoted entirely to the cause of fuel efficiency and economy. In stepping into the breach the Federation of British Industries is inspired with one idea—that of helping to form and guide a healthy public opinion on the general question. Differences of view as to ways and methods there will assuredly be, but none, we venture to believe, as to the fundamental truth that close attention to these problems is vital to the success of our trade at home and abroad.

In this and in any future issues of the *Review* that may be made—it is hoped that it may be possible to produce it at quarterly or other regular intervals—the endeavour is and will be to publish the views only of those qualified by experience in the various processes which present possibilites of fuel economy. The publication of the advertisements of makers of various appliances and devices for economising fuel consumption and of patent fuels will, it is believed, render the *Review* of greater practical value to consumers, but members and others will understand that these are accepted and inserted in the ordinary course of business.

We should welcome criticisms and suggestions regarding this new venture, especially those dealing with material for further issues which, it is hoped, will focus in detail new improvements in practice and plant for power raising.—*The Federation of British Industries Fuel Economy Review*, April, 1921.

## THE DEMAND FOR PATENT MEDICINES IN INDIA.

### Most Lines Saleable—An Increasing Demand—An Opening for Medicine Chests.

By GEORGE CECIL.

*Enterprise.*

With the growth of the white population of India, a large demand for patent medicines has arisen. Each year sees fresh manufacturing and commercial enterprises and the construction of railway lines undertaken, with the result that employment is found for managers, engineers, and foremen who are brought out from England—each of whom keeps certain patent medicines in his bungalow. Nor is the Eurasian (half-caste) element behindhand in following the example set by the "Sahib": every year they recognise more fully the necessity for having a cure on the premises, and provide themselves with various patent medicines, some of which, being of native manufacture, are of doubtful value. It will thus be seen that the demand is on the increase. For though Anglo-Indians die off from cholera, fever, and other ills peculiar to an unhealthy climate, the birth rate more than balances the mortality. The Englishman usually has his quiver full, while the half-caste's family invariably is out of all proportion to the parent's income.

*Blessed by the Priests.*

But it is not only amongst the Europeans and the Eurasians that the Anglo-Indian chemist finds his customers. The craze for education has spread to India, with the result that the native copies the manners and customs of the white man, even to patronising the same medicines. Thirty years ago the coloured person who suffered from rheumatism used poultices of leaves, the healing properties of which were vouched for by the priests; now-a-days he buys a bottle of something

efficacious. His father was content to suffer toothache; the son sends an order to the nearest chemist for some patent "pain-killer," taking care to explain that an imported article of European manufacture is required. In this connection, the down-to-date native has a supreme contempt for "country-made" concoctions He imagines that the ingredients are of an inferior quality, and that though the medicine costs less, it cannot have the same effect as (what he is pleased to term) "Europe Goods." When writing his requirements, the educated native often expresses himself in an extraordinary manner, as will be seen from the following example, the original of which was written by a Mahometan schoolmaster in Lucknow:—

"Sir,—Please to send me instanter by the fellow who brings this letter a little phial of the headache pillules as you supply to the European ladies and gentlemen of the station they must be Europe Goods I am not liking native trash so please note I think they have for name phenactin bayer and the proportions must be as per accustomed thing I will pay you the cash system if you will make me the due discount and for this I will ever pray for your prosperity, and present and future offspring. Yours sincerely,

— ———, B.A. of Calcutta University
Lucknow. and etc.

*Native Establishments.*

Although the import business is chiefly confined to India's European chemists, there are a number of Parsee and native concerns which devote a department to drugs. Such establishments are to be found all over the country, and a fair proportion of them, especially the Parsee firms, can be trusted by the manufacturer to meet their obligations in an honourable manner. The small native concerns are less satisfactory, for the proprietors are continually in financial difficulties; their profits are cut; the outstandings are far in advance of the collections; and the only good customers in the place fight shy of them. As to the Eurasian chemists, they are practically hopeless. Starting business without the necessary amount of capital, they are too lazy and stupid to conduct their affairs in a sensible manner; and they fail to command the confidence of the English and native community, or even that of their fellow half-castes. These people are best left to the big Calcutta and Bombay wholesale chemists; being on the spot, they can satisfy themselves as to the standing of the would-be customer and arrange accordingly. But an effort might be made to do business direct with the large Parsee, Mahometan, and Hindoo chemists and general shopkeepers, who either purchase in India or indent on an East India merchant or agent—who charges them a commission. The native is a keen man of business, and readily appreciates any economy in buying.

The majority of the lines which meet with a sale at home are popular in India. Bromo seltzer, phenacetin, and caffeine tabloids, menthol, and other remedies for headaches which arise from worry, are always in demand. Beecham's Pills are as well known, and as greatly appreciated, as anywhere in Christendom; embrocation is used in eight out of ten Anglo-Indian stables; emulsion is prescribed for many a white man and woman who is the worse for a "hot weather"; and chlorodyne, liver pills, and other equally well-established remedies have a large sale. But there is no need to add to the list; it is sufficient to say that the existing demand is a large one, and that it gives every promise of increasing year by year.

*Value for Money.*

The manufacturer must remember that both Anglo-Indians and natives strongly resent any (supposed) attempt on the part of a chemist to get the better of them. If they buy an "instantaneous headache cure" they expect to lose the headache in five minutes! They are not satisfied with the printed instructions which provide for "another dose if necessary in half-an-hour"; they argue that the medicine professes to rid them of the headache at once, and that the chemist has "done" them. Nor is this the worst, for (having little to do and plenty of time in which to do it) they babble to their acquaintances of their woes, and do their best to give the remedy a bad name. In a few days nearly eveyone in the "station" knows that the "instantaneous headache cure" or "toothache cure," as the case may be, does not fulfil its promise—with the result that the unfortunate chemist is left with so much dead stock on his hands. This damage done by ill-chosen names and carelessly worded instructions is far greater than the reader probably imagines; it may deprive a supplier of a valuable account and seriously interfere with the sale of the article all over India.

There is also a satisfactory demand for japanned tin medicine chests, tin being preferable to leather on account of the dampness of the rainy seasons. These must be as compact and portable as possible, and should contain, say, a carefully-chosen assortment of patent medicines suitable for a country in which intermittent fever, ague, cholera, and headache are rife. Particular care must be taken to make both the medicine chest and the phials as near air-tight as possible.

It is not only in India that enquiries for patent medicines are on the increase. In Cairo, Alexandria, Port Said, Aden, Colombo, Penang, Singapore, throughout Burmah, and in fact, everywhere in the East, they have an excellent sale. This more particularly applies to the well-established articles already mentioned. But conservative though the European and native chemists are, they often recognise that the new article which they can sell at a high rate of profit is well worth the pushing necessary to make it as successful as the better-known line with which it competes.

10 Rue Châteaubriand,
Paris, VIIIe.

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SOCIETE DES INGENIEURS CIVILS DE FRANCE.—A Summer Meeting of the British Section will be held in France between June 18 and 24 next. Members of the Faraday Society desirous of taking part in this meeting are invited to communicate at once with Mr. H. Sloog, 45, Great Marlborough Street, London, W.1, from whom full particulars may be obtained.

VISIT TO THE ROTHAMSTED EXPERIMENTAL STATION.—In connection with the General Discussion on Chemico-Physical Problems relating to the Soil at the Faraday Society, members and their friends are invited by the Director to visit the Rothamsted Experimental Station on June 1. A train leaves St. Pancras for Harpenden at 8.30

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

*Ordinary Meeting, May* 12, 1921.

Prof. C. S. Sherrington, President, in the Chair.

The following papers were read:—

"*The Problem of Finite Focal Depth revealed by Seismometers.*" By G. W. Walker, F.R.S.

Observations of the emergence angle of P waves at Pulkovo suggest that the depth of focus is of order one-fifth of the earth's radius. It is shown that important modifications would have to be made in the interpretation of seismograms and in the attempt to determine how speed of propagation depends on depth. It is further shown that an important test of the accuracy of the Pulkovo values can be made by a careful scrutiny of seismograms for distances > 11,000 kilometres. Further progress cannot be made until this research has been carried out, and until we have corresponding measures of the angle of emergence of S waves by means of three component seisometers.

"*A Liquid Oxygen Vaporiser.*" By E. A. Griffiths.

The liquid oxygen is contained in a metal vacuum vessel. The emission of gas is governed by bringing a flexible portion of the outer wall into contact with the inner: the degree of contact determining the rate of transmission of heat across. The bottom of the outer vessel is a corrugated plate of silver, to the centre of which is soldered a copper block shaped to fit the contour of the inner vessel. The displacement of the diaphragm is controlled by a screw. Any desired rate of gas evolution can be obtained up to 10 litres per minute, and the delivery remains constant with any particular setting for several hours.

The apparatus was designed in the course of experiments carried out with the Tyndall Mining Research Studentship of the Royal Society.

"*Some Experiments on the Catalytic Reduction of Ethylene to Ethane.*" By Dorothy M. Palmer and W. G. Palmer.

The hydrogenation of ethylene in the presence of nickel has been quantitatively examined. The mixture of ethylene and hydrogen under investigation was brought into contact with the nickel in an electrically-heated tube, so arranged that the catalyst was in constant motion through the gas.

The rate of hydrogenation was measured by the rate at which the mixture of ethylene and hydrogen in equal proportions by volume had to be passed into the tube to maintain the gas therein at constant pressure.

The effect of varying the proportions of the two gases at constant reaction temperatures, and of varying the temperature for a reacting mixture of constant proportions were separately elucidated.

The curves showing rate of reaction against time from the beginning of the experiment show "induction" periods (during which no hydrogenation took place) varying in duration from a few seconds to many hours according to the conditions of the experiment.

At the end of this period the rate of reaction increases rapidly to a sharp maximum, and then decreases less rapidly to a lower value, which only slowly decreases with time. A theory is advanced to account for these effects.

"*The Catalytic Activity of Copper.*"—*Part II.* By W. G. Palmer.

The apparatus used in the experiments and some preliminary results for which hydrogen was used to prepare the catalyst from cupric oxide were described in *Proc. Roy. Soc.*, A, lxxxix., 13.

In the present paper the activity of the catalyst when prepared from oxide by reduction with carbon monoxide and methyl alcohol vapour is described and discussed. In addition to anhydrous ethyl alcohol, constant-boiling mixtures of the following alcohols with water were used as reactants: — ethyl alcohol, *iso*-propyl alcohol, *normal*-propyl alcohol. It is shown that water acts as a positive auxiliary catalyst, and hydogen as a negative auxiliary catalyst, when adsorbed on the copper. Water may be retained on the catalyst either by absorption from a reacting alcohol-water mixture, or as the result of preparing the catalyst from oxide with hydrogen or methyl-alcohol vapour.

The activity-temperature curves for a catalyst prepared by carbon monoxide are shown to obey a simple exponential law.

Between 270° and 280° C. the activity curves (except those for *iso*-propyl alcohol as reactant) undergo a sudden change of direction corresponding to a great reduction of the temperature coefficient. This is attributed to the diminution in the thickness of the adsorbed alcohol layer to at most two molecular diameters.

The activity of the catalyst does not increase continuously, as the temperature of its preparation from oxide is lowered. This result is discussed on the basis of a theory put forward in the previous paper.

"*The Total Heat of Liquid Carbonic Acid.*" By Prof. C. F. Jenkin and D. N. Shorthose.

The paper describes the measurements, carried out for the Engineering Committee of the Food Investigation Board, of the total heat of carbonic acid between temperatures of +10° C. and +100° C. and between pressures of 900 and 1800lb. per square inch. A full table is given of the values for every 5° C. and 100lb. per square inch. The results of these measurements show that the values hitherto accepted, which are based on the assumption that the specific heat at constant volume does not change over this range, require some correction, but not to any large extent.

"*The Viscosity and Molecular Dimensions of Gaseous Cyanogen.*" By A. O. Rankine, D.Sc.

1. The viscosity of gaseous cyanogen has been measured at two temperatures, 15° C. and 100° C., the values obtained being, respectively, $0{\cdot}896 \times 10^{-4}$ and $1{\cdot}264 \times 10^{-4}$ C.G.S. units. Assuming Sutherland's law of temperature variation, these data have been used to calculate Sutherland's constant (C.=280) and the viscosity at 0 C. ($\eta_0 = 0{\cdot}935 \times 10^{-4}$ C.G.S. units).

2. The mean collision area of the molecule of cyanogen has been deduced, —$1{\cdot}31 \times 10^{-15}$ cm.$^2$, which proves to be practically the same as that of a bromide molecule $1{\cdot}28 \times 10^{-15}$ cm.$^2$. This is consistent with the evidence so far available from crystal examination, for the molecular volumes of KBr and KCN are nearly equal, —4·31 and 4·28 respectively.

3. If X-ray crystal examination should prove what is usually stated, viz., that KCN and KBr are strictly isomorphous, the results here obtained are consistent with the Lewis-Langmuir view that the cyanogen molecule has a size and shape nearly the same as two nitrogen molecules linked together by sharing one pair of outer electrons.

## MANCHESTER LITERARY AND PHILOSOPHICAL SOCIETY.

AT the Annual General Meeting of the Society, held on April 26, 1921, the following officers and Members of Council for the session 1921-22 were elected :—

*President*—T. A. Coward, F.Z.S., F.E.S. *Vice-Presidents*—R. L. Taylor, F.C.S., F.I.C.; William Thomson, F.R.S.E., F.I.C.; Sir Henry A. Miers, M.A., D.Sc., F.R.S.; W. Henry Todd. *Secretaries*—H. F. Coward, D.Sc., F.I.C.; T. H. Pear, M.A., B.Sc. *Treasurer*—R. H. Clayton, B.Sc. *Librarians*—C. L. Barnes, M.A.; Wilfrid Robinson, D.Sc. *Curator*—W. W. Haldane Gee, B.Sc., M.Sc.Tech. *Other Members of the Council*—Arthur Lapworth, D.Sc., F.R.S., F.I.C.; C. E. Stromeyer, O.B.E., M.Inst.C.E., M.Inst.M.E.; W. M. Tattersall, D.Sc., Leonard E. Vlies, F.C.S., F.I.C.; F. W. Atack, M.Sc.Tech., B.Sc., F.I.C.; F. E. Weiss, D.Sc., F.R.S., F.L.S.; Francis Jones, M.Sc., F.R.S.E., F.C.S; Laura Start, M.A.; Sydney Chapman, M.A., D.Sc., F.R.S.; and *ex-officio* the Chairman and the Secretary of the Chemical Section.

The Annual General Meeting of the Chemical Section of the Society, held on Friday, May 6, elected the following :—

*Chairman*—Leonard E. Vlies, F.C.S., F.I.C. *Vice-Chairman*—J. H. Lester, M.Sc., F.I.C. *Hon. Secretary*—David Cardwell, M.Sc., F.I.C. *Committee*—F. W. Atack, B.Sc., M.Sc.Tech., F.I.C.; W. H. Bentley, D.Sc., F.C.S.; Harold Moore, M.Sc.Tech., F.C.S., A.I.C.; Rona Robinson, M.Sc., A.I.C.; T. Roland Wollaston, M.Inst.Mech.E.; Edward Ardern, D.Sc., F.I.C.; R. H. Clayton, B.Sc.; J. E. Myers, O.B.E., D.Sc.; and D. M. Paul, B.Sc., A.I.C.

# CORRESPONDENCE.

## WATER AND ICE.

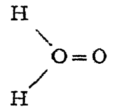
*To the Editor of the Chemical News.*

SIR,—I have been reading the articles on "Water and Ice" with interest. I have noticed in the Eastern Mediterranean that the shadow of the vessel on the water which in direct sunlight is a beautiful blue, is of a dark purple colour. This is due, no doubt, to slanting rays from the illuminated body, and forms part of the absorption spectrum.

As regards the colour of the sky, it seems by its purity to be due to particles which are molecular or sub-molecular in size—electrons in association with oxygen, *cp.*, the blue of ozone.

Physical properties like molecular refractions cannot give us any information regarding the degree of complexity of the water molecules for the following reason :—

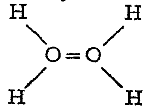
Hydrogen peroxide



o′ 1·76

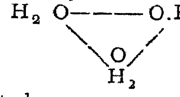
o″ 2·24

Water Dihydrone



o 1·76

Trihydrone

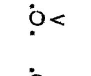


o 1·76

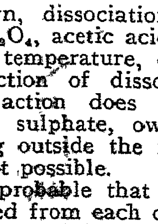
Unsubstituted oxygen possesses an atomic refractivity of 2·24; substituted oxygen one of 1·76 The positive hydrogen seen to absorb the unsaturation of the doubly tinted oxygen or cause a refraction of the oxygen electrons. These are the hydrones, according to H. E. Armstrong. The hydrols contain singly-linked tetravalent oxygen with an atomic refractivity of 1·76, *cp.*, the ozonides of Harries.

The hexacyclic formulæ for water, &c., and the conditions in hydrated copper salts, &c., also in my opinion, exclude full tetravalent function for oxygen. According to Rooseboom's theory and observations, the various molecules of water come away in groups, the members of one group all a one temperature, which is thus like a boiling point depending upon loose molecular association or particles under constant pressures.

These conditions resemble those for molecular associations, but not combinations, and are those for the manifestation of absorption spectra

compare  (coloured)

There is no need to suppose the necessary want of validity of the formulæ (as such). The conditions would resemble a series (rings or otherwise) of magnets separated by an air or other dielectric space. The opposed electrons might be



the cause of the blue colour.

As is well-known, dissociation of true chemical complexes like $N_2O_4$, acetic acid, take place over a wide range of temperature, due, of course, to the balancing action of dissociated molecules This balancing action does not exist in dehydrating copper sulphate, owing to the water molecules passing outside the range. In water and ice this is not possible.

It thus seems probable that the oxygen molecules are separated from each other by a shell of dielectric, and the valencies are activated, but not united, or only very loosely. It would be interest

ing to find out how many degrees of association there may be without combination. In any case, what is the exact connotation of this term?

It is, however, evident that in copper and other salts all the water molecules are not in equal degree of association with the metallic extra valencies, thus showing the existence at different distances from the metallic centres.—I am, &c.,

Gervaise Le Bas.

P.S.—A study of the dielectric constants, refractivities of some of the compounds mentioned might prove of value.

6, Springfield Crescent,
St. Heliers, Jersey.

## SALARY OF CHEMISTS.

*To the Editor of the Chemical News.*

Sir,—With reference to the article which appeared in your issue of May 6, entitled "The Present Position of Chemistry and Chemists," by Prof. Wilsmore, I have written to him pointing out an error in his Address. The statement that the Research Department, Woolwich, advertised for chemists with the qualifications and at the salary mentioned in his Address is incorrect. No such advertisement was issued by that Department, which at that time was offering for chemists a much larger salary. As is well known, it has since been successful in obtaining a scale of pay for chemists which is considered satisfactory by chemists themselves.—I am, &c.,

R. Robertson

29, Charlton Road,
Blackheath, S.E 2.

## PAPERS RECEIVED.

"Atomic Energy and Radiation." By F. H. Loring. Received May 17, 1921.

"A Method for the Rough Estimation of Iron and Manganese in Systematic Qualitative Analysis." By L. J. Curtman and N. H. Hecht.

The new method which is proposed in this paper for the rough determination of iron, is based on the fact discovered by one of us (L.J.C.) that ferric thiocyanate may be bleached by a solution of $SnCl_2$. In volumetric methods for the determination of iron, the usual procedure is first to reduce the iron and then to oxidise it with a standard solution of an oxidising agent. Our method follows the reverse order: the iron, if not already in the ferric condition is first oxidised, treated with KCNS, and then reduced with a standard $SnCl_2$ solution. The results obtained by this method were so surprisingly accurate that we undertook a special study of the procedure to determine whether or not it could be used as a substitute for the standard volumetric methods. The details of this procedure, together with data showing how the new method compares with the old standard procedures will shortly be reported in another communication. In the rough estimation of manganese, the latter is oxidised by sodium bismuthate in a nitric acid solution to permanganic acid, which is then estimated volumetrically by means of a standard solution of hydrogen peroxide.

## NOTES.

Theory of Relativity.—A Lecture will be given at King's College on Thursday, June 9, at 5.15 p m. by Professor Einstein on "The Development and Present Position of the Theory of Relativity." The Chair will be taken by Viscount Haldane. A charge of 2s. 6d. will be made for admission, and the proceeds will be given to the Imperial War Relief Fund. The Lecture will be delivered in German. Tickets can be obtained on application to the Lecture Secretary.

Royal Institution.—On Tuesday next, May 31, at 3 o'clock, Sir James Frazer delivers the first of two lectures at the Royal Institution on (1) "Roman Life in the Time of Pliny the Younger," and (2) "London Life in the Time of Addison." On Thursday, June 2, Sir Alexander Mackenzie begins a course of two lectures on "Beethoven" (with musical illustrations), and on Saturdy, June 4, Mr. R. S Rait gives the first of two lectures on (1) "Scotland and France" and (2) "Scott and Shakespeare." The Friday Evening Discourse on June 3 will be delivered by Dr. Leonard Huxley, Editor of the *Cornhill Magazine*, on "Chronicles of the Cornhill," and on June 10 by Dr. A. G. Webster on "Absolute Measurement of Sound" An extra Discourse will be delivered on June 17 by Sir J. J. Thomson on "Chemical Combination and the Structure of the Molecule."
a.m.

The British Engineers' Association.—The Annual General Meeting of the British Engineers' Association took place at 32, Victoria Street, London, S.W.1, on Thursday, May 12. At a meeting of the Council of the Association that followed, Mr. Nevile Gwynne, late Chairman of the Executive Committee, was elected President of the Association, in place of the retiring President, Col. O. C. Armstrong, D.S.O., who had occupied the position of President for three years, and to whom a very hearty vote of thanks was accorded. Mr. E. W. Petter was elected Chairman of the Executive Committee in succession to Mr. Nevile Gwynne.

## New Patents.

This List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W.C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

12901—Aluminium Industrie Akt.-Ges.—Process for manufacture of nitrate of calcium. May 5th.

13004—Blagden, J. W—Manufacture of amino derivatives of hydro-genated cinchona alkaloids and their derivatives. May 6th.

12984—Frischer, H.—Apparatus for carrying out chemical and physical processes. May 6th.

*Specifications published this Week.*

162314—Pease, E. C.—Extraction of ammonia from gases.

138129—American Coke and Chemical Co—Ammonia saturators.

162578—Friederick, W.—Process for the mannfacture of trinitrorsorcine.

*Abstract Published this Week.*

*Synthetic Resins.*—Messrs. Vicker and The Ioco Rubber & Waterproofing Co., of Anniesland, Glasgow, has obtained a Patent No. 160258 for some improvements in the preparation of Phenol

aldehyde condensation products. In the condensation of phenolic bodies with aldehyde compounds, the catalyst employed is a salt or double compound of hexamethylene-tetramine or mixtures of these, employed in such proportions that the quantity of hexamethylene-tetramine contained therein does not exceed 2 per cent by weight of the reacting ingredients Examples of the salts of hexamethylene-tetramine are the chloride, sulphate, acetate, tartrate, citrate, benzene sulphonate, toluene-p-sulphonate, camphorate, arsenate, trimetaborate, salicylate, sulphosalicylate, phthalate, perchlorate, chromate, sulphocyanide and tannate. Examples of the double compounds are those with phenolic bodies, such as phenol, resorcinal, pyrogallol, and guaiacol, or with halogenated compounds, such as ethyl bromide, chloral, bromine iodide, ethyl iodide, and iodoform; or with metallic salts, such as aluminium acetate, potassium antimony tartrate, sodium acetate, ferric chloride, and mercuric chloride According to the provisional Specification, hexamethylenetetramine itself may be employed as the catalyst.

Hexamethylenetetramine Salts—The acetate benzene sulphonate, and tuene-p-sulphonate of hexamethylenetetramine are prepared by evaporating equeous solutions of the base and the respective acids, preferably in vacuo, and purifying the products by crystallization from alcohol.

Messrs. Rayner & Co, will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

## MEETINGS FOR THE WEEK

*Monday, May 30*

Royal Society of Arts, 8. "Industrial Disease and Immunity" by Sir Kenneth Goadby.

*Tuesday, May 31.*

Royal Institution, 3. "Roman Life" by Sir James Frazer.

Faraday Society, 4.30. General Discussion on "Physico-Chemical Problems relating to the Soil".

Institution of Electrical Engineers. Annual Meeting, at 5. At 6.30, "Research Work in the United States" by Dr. F. B. Jewett.

*Wednesday, June 1.*

Society of Public Analysts, 8. "Composition of Egg Powder" by F. F. Beach, T. E. Meade and E Russell. "The Colorimetric Method of Determining H ion Concentration. Some Uses in the Analytical Laboratory" by Norman Evers. "Estimation of Woody Fibre in Cattle Food" by F. Robertson Dodd.

*Thursday, June 2*

Royal Society, 4.30. (Bakerian Lecture). "Optical Rotatory Dispersion" by Dr. T. M. Lowry and Dr. C. P. Austin.

Chemical Society, 8.

Royal Institution, 3 "Beethoven" by Sir A. C. Mackenzie.

*Friday, June 3.*

Royal Institution, 9. "Chronicles of the Cornhill" by Dr. L. Huxley.

*Saturday, June 4.*

Royal Institution, 3. "Scotland and France" by Robert S. Rait.

## NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemical Apparatus, &c., for review or notice to be addressed to the Editor.

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THE CHEMICAL NEWS,
97, Shoe Lane, London, E.C 4.

THE CHEMICAL NEWS.

VOL. CXXII, No. 3190.

## LABOUR AND DISILLUSIONMENT.

ANOTHER milestone has been reached and passed by the Industrial League; not the milestone of space, but one epoch marking in the annals of that organisation. It hove into sight, if one may so use the term, but a few weeks ago, when it was learned that the election of the Rt. Hon. J. H. Whitley, M.P., to the Speakership of the House of Commons rendered it incumbent upon him to resign the Joint Presidency of the League, and it was passed on May 19, when Viscount Burnham, the new Joint President with the Rt. Hon. G. H. Roberts, M.P., was the central figure in a happy reception held by the Executive Committee at the Eccentric Club, Ryder Street.

The dinner was presided over by the Rt. Hon. G. H. Roberts, and in addition to Viscount Burnham there were present Sir Wm. Wayland (Messrs W. A. Wayland & Co.), Sir John Prestidge (Messrs. J. Stone & Co., Ltd.), Sir Hy. Birchenough, Mr. G. J. Wardle, C.H., Mr A. Bellamy (Ex-President National Union of Railwaymen), Mr. A. Allison (Asbestos and Cable Workers' Union), Mr. Hugo Hirst (General Electric Co., Ltd.), Mr. D. Gilmour (Metalliferous Miners' Union), Mr. J. F. Green, M.P., Mr. H. Scholey (Messrs. Scholey & Co., Ltd.), Mr. H. V. Roe, Mr. W. S. Bishop (Mayor of Lambeth), Mr. E. E. Eccles and Mr. A. Jacob (British Aluminium Co.), Mr. H. S. Horne (Messrs. Read & Brigstock, Ltd.), Mr. M. W. Reid (National Foremen's Association), Major A. Vigor (Messrs. A. Vigor, Ltd.), Mr. Lee Murray, Col. Meurling, Mr. J. Murrey (National Federation of Building Trade Operatives), Mr. Frank Smith (Shipbuilding Trades' Federation), &c.

The Rt. Hon. G. H. Roberts, M.P., in proposing the toast "Our Guest, Viscount Burnham", made some candid remarks relative to the industrial situation. The League felt, he said, that in securing the adhesion of Lord Burnham they were starting a new era, not to bring aggrandisement to individuals, but stability, integrity, and greater prosperity to the nation. They needed an informing and steadying influence in their midst. It was not the correct thing to give too much credence to the operations of disruptive forces in their midst, but he declared that they should not be ignored, for the Red scourge was like corrosive poison, constantly undermining our social fabric, just as the White scourge was constantly ravaging humanity. Unless they applied correctives to meet that social mischief, the whole edifice would be unable to withstand any sudden attack which might be made upon it. Since the war, strike had succeeded strike, with the result that those who pinned their faith to the Labour party found themselves now disillusioned—a disappointment and disillusionment that they would not get over within the lifetime of any of those present. The working classes of this country, unwittingly, had in the main created the evils and want that existed throughout the land. They had been misled by false leaders, and therefore, it was felt that the Industrial League was needed more than ever. They wanted the society of men like Lord Burnham, whose contribution would be helpful. The coal strike had been protracted, not because of the merits of the case, but because the miners' leaders had been afraid to tell the rank and file the truth. Neither this country nor any other could uphold industries which could not maintain themselves. No industry could be definitely bolstered up simply by falling back upon the general taxation of the country. It should be the duty of leaders to educate the rank and file, otherwise they forfeited the right, if they ever had the right, to be recognised as leaders. Not only in the miners' unions, but in almost every trade union of the country, the membership was declining, and the trade union movement would, at the end of this experience, be so weakened that it would cease to be an effective force for a generation. That, to him, would be lamentable, because he believed in trade unionism. On the other hand, he also believed that employers could be successful only by operating together. The weakening of trade unionism was not the result of a conspiracy on the part of wicked capitalists. It had been wrought from within, by people who were not concerned to uplift the workers, or were not interested in the integrity and greatness of Great Britain, but who were pursuing a spurious nationalism founded on the belief that the interests of all nations were identical, and that Great Britain ought to sink back in order to allow other nations to destroy her.

MR. HUGO HIRST, supporting the toast, congratulated the League on acquiring the services of Viscount Burnham, who, he said, had done much to alleviate distress and to bring wise counsels and compromise to bear in industrial disputes. He could not imagine a greater asset to the League than the acquisition of such assistance.

VISCOUNT BURNHAM, in responding, said this League embodied the spirit of the round table—a table without sides and without corners. (Cheers) It stood for good sense, and good feeling in the industrial life of the country; it was the sworn friend of social goodwill, the sworn enemy of economic dogmas. They all felt that it was not enough to indulge in pleasant platitudes and say that they regarded the class war as the abominable thing. What they had to do was to establish the rule of reason. What we suffered from to-day was fanaticism—not on the part of the masses, but on the part of some of the leaders they blindly followed. Therefore, they should turn to account the great qualities of British character, of which loyalty was a conspicuous feature. Loyalty to a cause, or even to a great party, was always eulogised as being a civic virtue, and yet they were suffering to-day from an excess of loyalty on the part of large bodies of their fellow-countrymen to great industrial organisations which they did not wish to be charged with betraying.

SIR WILLIAM WAYLAND proposed a vote of thanks to the Chairman, Mr. G. J. Wardle, M.H., and Sir Henry Birchenough also supported. Mr. ROBERTS ably responded.

# A METHOD FOR THE ROUGH ESTIMATION OF IRON AND MANGANESE IN SYSTEMATIC QUALITATIVE ANALYSIS

By L. J. CURTMAN and N. H. HECHT.

*Procedure.*

The Group III. precipitate consisting of the hydroxides of Al, Cr, and the sulphides of Ni, Co, Fe, Mn, and Zn is treated with 60-80 cc. of HCl (1-9) and the NiS and CoS filtered off. The filtrate containing the Al, Cr, Fe, Mn, and Zn as chlorides is carefully evaporated to 2 cc. to remove the $H_2S$ and excess of HCl. It is then quantitatively transferred to a 50 cc. graduate, the dish rinsed several times with water and the volume in the graduate diluted with water to 50 cc. After thoroughly mixing, one-half of this solution is taken for the determination of Fe, and the other half for the estimation of Mn.

*Determination of the Iron.*—In a casserole treat 25 cc. of the above solution with 10 cc. 6N NaOH and 1·5 grm. $Na_2O_2$ Boil the mixture with constant stirring for several minutes to decompose the excess of $Na_2O_2$. Dilute the solution with twice its volume of water, to prevent the swelling of the filter paper, and filter. Wash the precipitate with hot water. Treat the precipitate and filter in a beaker with 50 cc. of concentrated HCl, and immediately (Note I.) heat to boiling; when solution is complete, dilute the solution and filter off the paper. Wash the filter several times with dilute HCl. In an open Erlenmeyer flask boil down the combined solution and washings to about one-half the original volume to drive off any chlorine which may be present (Note II.). Cool (Note III.) the solution to room temperature, add 5 cc. 5*N* KCNS, and titrate the solution with $SnCl_2$ solution (containing about 5 mgrms. Sn per cc (Note IV.) to a pink colour (Note V.) which matches that of a solution containing 0·05 mgrm. Fe as $FeCl_3$ in 50 cc. HCl (1 : 1) and to which 5 cc. of 5*N* KCNS have been added. Unless special provision is made to exclude the oxygen of the air, it is necessary to standardise the $SnCl_2$ solution for each determination (Note VI.). This is best done by running a definite volume of a standard solution of $FeCl_3$, oxidised Mohr salt, or ferric alum, along with the determination. The presence of manganese does not interfere with the determination.

*Determination of the Manganese.*—In the other half of the solution, the Fe and Mn are precipitated with NaOH and $Na_2O_2$, and the mixture boiled, diluted, filtered, and washed. The procedure up to this point is identical with that given for the determination of iron except with regard to the washing of the precipitate. In this case the washing must be repeated until the precipitate is free of chlorides, since the latter interfere with the final determination. In a beaker treat the precipitate and filter paper with a mixture of 25 cc. of concentrated $HNO_3$ and 10 cc. of 3 per cent $H_2O_2$, heat to boiling, and when solution is complete, dilute and filter off the filter paper. Wash the filter and boil down the combined solution and washings in an open Erlenmeyer flask to about one-half of the original volume. Cool and transfer the solution quantitatively to a 100 cc graduated cylinder and dilute with water to the 100 cc. mark. Mix thoroughly, and take 20 cc. for the determination (Note VII.). Adjust the acidity of the 20 cc. portion by first neutralising with $NH_4OH$, adding 10 cc. concentrated $HNO_3$, and diluting the whole to 200 cc. Add 4 grms. of sodium bismuthate (Note VIII.), stir the mixture allow to settle for 5-10 minutes, and filter by decantation through a fluted filter. Wash the residue of sodium bismuthate in the beaker with 5 per cent $HNO_3$, and filter by decantation. The final volume will be between 250 and 300 cc. Titrate with 0·3 per cent $H_2O_2$ to a colourless end point. The $H_2O_2$ may be standardised by determining the quantity necessary to react with a definite volume of a standard $KMnO_4$ solution to which 1/4 of its volume of $HNO_3$ (Note IX.) has been added before adding the $H_2O_2$.

*Notes.*

I. It was found that when the mixture of $Fe(OH)_3$ and $MnO_2 \cdot XH_2O$ was allowed to remain in concentrated HCl overnight, a deep red solution was obtained even when only a small amount of Fe was present. The red colour was undoubtedly due to the Mn, for it was observed that the red colour deepened as the proportion of Mn increased. To avoid the formation of a red solution which would interfere with the subsequent determination of Fe, it is necessary to heat the mixture to boiling immediately after the addition of the HCl. Under these conditions, the colour of the solution changes from an opaque greenish black to a transparent yellow.

II. The chlorine results from the action of HCl on the hydrated manganese dioxide.

III. The solution must be cooled to room temperature, as otherwise there is danger of the $Fe(CNS)_3$ decomposing and giving a brown-coloured end point.

IV. The $SnCl_2$ solution may be prepared by dissolving 9·45 grms. $SnCl_2.2H_2O$ in 500 cc. concentrated HCl and diluting the resulting solution to a litre.

V. When attempts were made to titrate to a colourless end point, discordant results were obtained due to the difficulty of reaching the exact end point. This condition arises from the fact that the reaction proceeds very slowly as the end point is approached, and as a consequence, large intervals of time would have to be allowed between successive drops, added near the completion of the reaction, in order to determine the exact end point. Such a procedure was found impracticable. It has therefore seemed best to add the $SnCl_2$ quickly at the beginning of the titration until the solution (opaque at first) becomes transparent. When this stage has been reached, the $SnCl_2$ is added drop by drop, and the solution stirred vigorously for 10-20 seconds after each drop to determine whether the last drop has brought the end point. It was observed that solutions which had been completely titrated, slowly turned reddish on standing for from 5 to 10 minutes. This reddish colour which first formed on the surface of the solution was doubtless due to atmospheric oxidation.

It is more convenient in routine qualitative work to use for the titration of the Fe and Mn a 10 cc. graduated pipette instead of a burette.

VI. That a $SnCl_2$ solution rapidly changes owing to atmospheric oxidation is shown in the following instance. A freshly-prepared solution

of $SnCl_2$ when used as described in the method was found to be of strength 10 mg. Fe=2 cc. of $SnCl_2$. After being kept for 18 days at room temperature in a glass-stoppered volumetric flask, but with 300 cc. of air above the solution, it was again tested and found to be of strength 10 mgrms. Fe=5·8 cc. of $SnCl_2$. The solution was now only 1/3 of its original strength.

VII. An aliquot part is taken because the largest quantity of Mn that is likely to be present in 1 grm. of ore or in 0·5 grm. of an alloy is 500 mgrms. It was found that a solution of $HMnO_4$ whose Mn content exceeded 50 mgrms. in 200 cc. quickly decomposes. An aliquot part of the solution is therefore taken to make sure that the concentration is not too great. If 40 cc. are taken instead of 20, and all the quantities in the directions which follow are doubled, the final volume of the solution containing the Mn as $HMnO_4$ will be 400 instead of 200 cc. A little more than half of the solution is now filtered on a dry filter, and exactly 200 cc. of the filtrate is collected and titrated. This procedure is shorter than the one given, inasmuch as it makes unnecessary the filtration of the entire volume of the solution and the washing of the residue.

VIII. The sodium bismuthate (reagent grade) which was used was found to contain a small amount of Mn. It is therefore advisable to run a blank on a 4-grm. sample of the bismuthate in a volume of 200 cc.

IX. The presence of $HNO_3$ is necessary to prevent the separation of $MnO_2$. Pure $KMnO_4$, if accurately weighed, dissolved, and diluted in a volumetric flask, will yield a sufficiently reliable standard.

*Confirmatory Experiments.*

I. *The Relation between the Amounts of Iron Present and the Quantities of $SnCl_2$ used.*—Varying amounts of a standard solution of $FeCl_3$ were introduced into separate beakers. To some, 500 mgrms. of Mn as $MnCl_2$ solution were added. To each, 25 cc. of concentrated HCl were added, and the solution in each case diluted to 50 cc. After treating each solution with 5 cc. $5N$ KCNS and thoroughly mixing, the solutions were titrated with $SnCl_2$ solution to a faint pink end point. The results and other data are given in Tables I. and II.

TABLE I.

| Sol. No. | Mg.Fe | Mg.Mn | c. $SnCl_2$ used. | Appearance of the solution before titration |
|---|---|---|---|---|
| 1 | 100 | 0 | 18·01 | Opaque red |
| 2 | 50 | 500 | 8·88 | Opaque red |
| 3 | 25 | 0 | 4·38 | Opaque red |
| 4 | 20 | 500 | 3·50 | Opaque red |
| 5 | 10 | 0 | 1·60 | Opaque red |
| 6 | 5 | 0 | 0·76 | Transparent, blood red |
| 7 | 1 | 500 | 0·14 | Transparent, blood red |

TABLE II.

| Sol. No. | Mg.Fe | Mg.Mn | Cc. $SnCl_2$ used. |
|---|---|---|---|
| 1 .. | 1 | 250 | 0·60 |
| 2 ... | 5 | 250 | 2·92 |
| 3 ... | 10 | 250 | 5·80 |
| 4 ... | 100 | 0 | 61·70 |

In the experiments of Table II., the $SnCl_2$ solution was weaker than that used in the tests given in Table I.

*Conclusions.*—The results in Tables I. and II. lead to the following conclusions: (1) the volume of the $SnCl_2$ used is proportional to the amount of iron present; (2) manganese does not interfere with the reaction.

II. *Determination of Mn in Pure $Mn(NO_3)_2$ Solutions.*—Different volumes of a standard $Mn(NO_3)_2$ solution were treated by the procedure given for Mn except that the preliminary precipitation with NaOH and $Na_2O_2$ was omitted. The results are given below in Table III.

TABLE III.

| Vol. of conc. $HNO_3$, 10 cc. Sol. No. | Mg Mn | Total Vol. of the Solution 200 cc. Cc. of $H_2O_2$ used. |
|---|---|---|
| 1 | 50 | 30·00 |
| 2 | 25 | 14·96 |
| 3 | 20 | 12·34 |
| 4 | 10 | 6·02 |
| 5 | 5 | 2·89 |
| 6 | 1 | 0·59 |

The above results show that the volume of $H_2O_2$ used is proportional to the quantity of manganese present.

III. *Determination of Iron and Manganese by the Procedure.*—To test the relability of the proposed method for the rough estimation of iron and manganese, a number of solutions containing definite amounts of Fe and Mn were analysed by the procedure given in the first part of this paper The results are given in Table IV.

TABLE IV.

| Sol. No. | Mg.Mn | Mg Fe | Cc. $H_2O_2$ Used. | Cc. $SnCl_2$ Used. | Found. Mg Mn | Found. Mg.Fe |
|---|---|---|---|---|---|---|
| 1 | 500 | 500 | 26·97 | 16·18 | 506 | 508·6 |
| 2 | 250 | 50 | 14·60 | 1·61 | 273 | 50 |
| 3 | 300 | 100 | 16·19 | 3·10 | 303·7 | 97·6 |
| 4 | 100 | 0 | 53·30 | — | For standardisation of $H_2O_2$ | |
| 5 | 0 | 100 | — | 6·35 | For standardisation of $SnCl_2$ | |

*Comments*—In making the calculations it is necessary in accordance with the procedure, to multiply the quantities of $SnCl_2$ used by 2, and the figures for $H_2O_2$ by 10. Experiment 4 supplies the data for the calculation of the strength of the $H_2O_2$ in terms of Mn; while the strength of the $SnCl_2$ in terms of Fe may be readily calculated from the figures in experiment 5. The results in the last column show that the method supplies a relable means of roughly estimating the amounts of manganese and iron in systematic qualitative analysis.

*Summary.*

1. A rapid method is proposed for the rough estimation of iron and manganese in systematic qualitative analysis.

2. The estimation of the iron is based on the property of $SnCl_2$ to bleach the deep red $Fe(CNS)_3$, formed by adding KCNS to the $FeCl_3$ solution.

3. The manganese is converted by sodium bismuthate in nitric acid solution to $HMnO_4$, and the latter bleached by the use of a standard solution of $H_2O_2$.

4. Since the presence of either metal does not interfere with the determination of the other, it is unnecessary to effect their separation in this method.

5. Test analyses show that the method is trustworthy.

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## THE PURIFICATION AND SOME PHYSICAL PROPERTIES OF CERTAIN ALIPHATIC ALCOHOLS.

By ROGER F. BRUNEL, J. L. CRENSHAW and ELISE TOBIN.

We have found it necessary to prepare in this laboratory a series of aliphatic alcohols, in which there should be, if possible, no impurity exceeding 0·1 to 0·2 per cent, and have undertaken to purify these alcohols by a somewhat more careful fractional distillation than is usually carried out.

A little examination of the literature will show that there is no criterion for the purity of any except a few of these simple substances. Except in the cases of methyl and ethyl alcohols agreement in boiling points to 0·1° and in densities beyond the third decimal is unusual. (Michael, Scharf, and Voigt (*Jour. Amer. Chem. Soc.*, 1916, xxxviii., 653); purified *iso*-butyl alcohol with great care, and Orton and Jones (*J. Chem. Soc.*, 1919, cxv., 1194), *n*-butyl alcohol, but the physical properties are not recorded. *Tertiary* butyl alcohol, by reason of its high melting point, has also probably been obtained pure.) Since the chief criterion of purity of our own products is in the data obtained in the distillation it appears necessary to enter into some detail with regard to the stills used, and even more, with regard to the fractions actually obtained, particularly since most common organic compounds have already been fractionated "with great care" by various investigators.

*Method of Distillation.*—The stills most used have been brass tubes (pyrex columns of the same height and 36 mm. in diameter have occasionally been used). 1·8 meters tall and 30 mm. in diameter, filled with quartz pebbles which pass through 4-mesh, but not 5-mesh wire netting. These pebbles, obtained under the name of Long Island grit, were cleansed with *aqua regia*, and all markedly pitted or flattened pebbles were picked out.

With alcohols boiling above about 80°, the condensation in such a column, even when wrapped with asbestos, is so great that the vapour can be driven up through it only with difficulty. The columns are therefore wound with resistance wire (a winding with Advance (constantan) wire, No. 21 gauge from the Driver-Harris Wire Co., six turns to the inch, is satisfactory with the 110 v. current) upon a layer of asbestos, and sufficient current is sent through to overcome some of the loss of heat to the air and keep the distillation in progress with a flame 3 or 4 inches high under the flask at the bottom. Alcohols boiling as high as 130° have thus been distilled. Furthermore, by connecting the heating coil to the 220 v. circuit at the end of the distillation, the column can be heated as hot as desired, and the liquid retained by the pebbles greatly reduced, usually to about 30 cc. Towards the end of this process the fractionating effect is, of course, diminished, but when the alcohol is pure, no change in temperature occurs until the liquid is nearly out of the column, when super-heating becomes markedly evident. This point is so well marked that there is never any doubt as to when it is reached.

The effectiveness of the stills is, of course, greater, the slower the rate of distillation. The rate is followed by observing the drops from the end of the adapter on the condenser. The speed of distillation rarely exceeds 40 drops a minute, and during the last few distillations of a pure product it is kept at 15 to 30 drops a minute. With a pure substance the temperature of the vapour should, of course, be independent of the rate of distillation, and this was found to be the case with a five-fold change in the rate with *iso*-propyl and *iso*-butyl alcohols. It appeared to be the case for all of the alcohols with the small changes in rate which inevitably occur.

The temperatures are read on thermometers graduated to 0·1°. With our tall stills it is impracticable to use a cathetometer, but a special reading device, magnifying five diameters, is supported against the still head in such a way that perpendicular vision is obtained, and errors due to parallax are avoided (A brass tube, 15 cm. long, with support to fit the still head, is fitted with a Bausch and Lomb 25 mm. triple aplanat lens as objective and a brass cap with 1·5 mm. hole as eyepiece. This device, in improved form, is now offered for sale by the A. H. Thomas Co., of Philadelphia). The temperature is always read to 0·01°, and the barometer read simultaneously. *When products are spoken of as constant boiling, constancy to* 0·01°, *as nearly as can be read, is to be understood.*

The thermometer is enclosed in a glass still head at the top of the column, 20 mm. in diameter, and tall enough so that the thermometer can be suspended completely in the vapour. A wire ring prevents contact with the walls. (The thermometer bulb was thus far below the side arm, but there is no reason to expect change of composition of the vapour in ascending the glass tube above such a tall column, except with impure substances and a device such as that of Richards and Barry (*Jour. Amer. Chem. Soc.*, 1914, xxxvi., 1787) appeared necessary). The immersion of the entire thermometer in the vapour is of the greatest importance with thermometers which are not gas-filled. If only the mercury stem is immersed, enough mercury distills and condenses further up the capillary to cause serious error in a short time (Olivier, *C.A.*, 1917, xi., 1927, has observed such vaporisation of the mercury in a thermostat at 30°). The bulb of the thermometer is protected from radiation by black paper around the glass. If there is any difference between the effect of such a shield and one of nickel or iron inside the still head, it is a matter of less than 0·005° at the temperatures here concerned. The chief purpose which the shield serves is to provide protection from radiation from nearby lights, which may raise the temperature of the thermometer some hundredths of a degree.

Our stills are sufficiently effective so that in many cases we obtain a considerable quantity of distillate within 0·01° after one or two distillations, but it is, of course, a more difficult matter to obtain products which will redistil entirely, or nearly entirely, at constant temperature

*The extent to which a constant boiling fraction finally again comes over at constant temperature is what we have taken as the chief criterion of purity.* Statements that "nearly all" of a product distils constantly appear so inexact that we have given below the boiling-point range and weight of the fractions in many of the final distillations,

and in all cases the percentage of the product collected without change of temperature.

Sometimes nearly the whole amount distils at constant temperature, but we have usually had to be satisfied when 70 to 80 per cent, and in a few cases even less of a product collected at constant temperature would again come over at the same temperature. In such cases the deviation from constancy has not been great. The distillation rarely begins more than 0·15° below the true boiling point, and frequently only a few drops come over so low. Sometimes the low boiling portions are all within 0·05 or even 0·2°. The temperature at which the distillation begins can well be determined since the hot vapour is at first driven up through the still head slowly, and the thermometer is deeply enough immersed to assume the temperature of the vapour before any passes over.

Since the temperature in the final distillations, when it has once become constant, always remains constant until the distillation ceases, it is evident that high boiling impurities are retained in the still, if they have not been already eliminated in the liquid retained by the still in earlier distillations. In the case of *iso*-propyl and *iso*-butyl alcohols the residues from distillation of a number of nearly pure specimens were united and subjected to further fractionation. Since these residues yielded, with very little further fractionation, specimens which did not differ in density or refractivity from the main products, it appears that high-boiling impurities were probably eliminated early in the process of fractionation

The exact determination of the boiling points of the alcohols was a matter of difficulty. At first the final distillation of each alcohol was carried out with a still head containing three or four thermometers. When the corrections were obtained for the thermometers the boiling-point readings agreed within 0·02° at temperatures below 100°, but above 100° no satisfactory results were obtained. Through the courtesy of the Bureau of Standards, it was then arranged that we should take specimens of the alcohols to the Bureau and determine their boiling points with a resistance thermometer. Here it was found that with small specimens of the alcohols in a boiling point apparatus no constant readings could be obtained when the violence of the boiling was altered. In particular, with the higher boiling alcohols the temperature always fell as the violence of boiling was increased. We were not in a position to continue the work there long enough to discover whether the cause of the difficulty lay in the alcohols or in the design of the boiling-point apparatus.

In order to continue the work in our own laboratory, since we were equipped with a potentiometer, a thermoelement was employed.

*The Thermoelement.*—A 12-junction copper-constantan thermoelement was constructed materially according to the directions of Adams (*Jour. Amer. Chem. Soc.*, 1915, xxxvii., 484), of No. 36 copper and No. 30 constantan ("Ideal" wire from the Electrical Alloys Co., of Morristown, N.J., was used), B. & S. gauge. The constantan wire was tested for homogeneity in order to have as small electromotive forces as possible set up at points other than the junctions, and a good deal of wire was rejected. Twelve 120 cm. lengths were selected with 30 cm. at one end and 25 cm. at the other as homogeneous as possible, the former ends being used for the hot junction. Satisfactory junctions were not obtained with ordinary solder, so they were brazed with silver solder in a small flame, with borax as flux. They were then dipped in enamel obtained from a wire insulating company, which was hardened by heating at 230°. The sets of hot and cold junctions were enclosed in glass tubes connected by rubber tubing.

A Leeds and Northrup potentiometer was used, but the coils were first tested, since we wished an accuracy of 1 microvolt in 70,000. No corrections of more than 5 $\mu$v. were found necessary.

Three Clark cells and two sets of 5 Weston cells served as standards (Hulett's directions were followed, *Phys. Rev.*, 1911, xxxii., 257). These were kept in a thermostat at 24·94° ±0·005°. The Clark cells differed by only 0·00004 v. almost from the start, and the relation between them within this range remained almost constant. When the Weston cells became constant, they also remained nearly as close together. The ratio between the Weston and Clark cells has remained exactly that found by Guthe (*Guthe*, Bur. Standards, *Bull.* 2, 1906, 33) and Hulett (Hulett, *Phys. Rev.*, 1911, xxxii., 276), $\frac{1\cdot0184}{1\cdot42040}$ at 25°, for several months.

The calibration data for the thermoelement were as follows. Cold junction at 0°. $Na_2SO_4.10H_2O$, transition point 32·384° (Dickinson and Mueller, *Jour. Amer. Chem. Soc.*, 1907, xxix., 1381), 15,779 $\mu$v. $SrCl_2.6H_2O$, transition point, 61·341° Richards and Yngve, *ibid.*, 1918, xl., 89), 30,814 $\mu$v. Water boiling point, 52,127 $\mu$v. at 760 mm. Naphthalene boiling point, 217·58° at 753·4 mm. (Jaquerod and Wassner, *J. Chem. Phys.*, 1904, ii., 52), 12,4459 $\mu$v.

These values do not fall on a curve, which can be represented by three constants. The three higher values have, therefore, been used, giving the equation,

$$E=470\cdot045t+0\cdot54892t^2-0\cdot00042t^3$$

which does not differ greatly from that of White (White, *Phys. Rev.*, 1910, xxxi., 162), or that of Adams and Johnston (Adams and Johnston, *Am. J. Sci.*, [4] 1912, xxxiii., 538).

The value calculated for the transition point of sodium sulphate from our equation is 15,785, instead of 15,779 found. This corresponds to an error of nearly 0·01°, but we are using the element in the temperature range 78-130°, and our equation probably does not introduce an appreciable error there. (The equation recommended by Adams (*J. Wash. Acad. Sci.*, 1913, iii., 469, $E=At+B(1-e^{-Ct})$ would very likely prove more satisfactory, but we have not, up to the present, had the necessary table of exponentials at hand).

The increase in e. m. f. per degree varies from 551 $\mu$v. at 77° to 654 $\mu$v. at 217°. Since it is readily read to 1 $\mu$v., the thermoelement is evidently sensitive to 0·002°. In fact, a change of 0·5 $\mu$v. is noticeable on the potentiometer. Although we believe that the boiling point of water is reproduced to better than 0·01°, such accuracy has not been obtainable with the alcohols, but most of these are probably correct to ± 0·01°.

The thermoelement is inferior to the resistance

thermometer for the determination of boiling points unless an instrument can be made which is independent of the depth of immersion in the hot vapour. In spite of our care in choice of the constantan wire, the e m. f. varied with the depth of immersion as much as 8 $\mu$v. at 100°, the greatest error occurring when just the tip was heated. But it was found that there was a range of about 7 cm. over which there was no change, and there was only about 3 $\mu$v. variation in the immediate neighbourhood of this region. The element was therefore used with an immersion of about 14 cm. with the possibility of varying this several cm. either way without altering the reading. (With naphthalene there was variation in the reading even within this best portion of the element. The calibration value was read with what we considered our standard depth of immersion).

A nickel or iron shield has been used about the thermoelement. We have not detected any difference between them. A piece of black paper outside the tube has the same effect to within 0·005°. The effect of omitting the shield depends mainly upon the surroundings, the thermoelement being sensitive to changes in the illumination of the room, such as the lowering of a shade in a window some distance away, or switching lights on or off within a metre or two of the apparatus.

(To be continued).

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

*Ordinary Meeting, May 26, 1921.*

Prof. C. S. SHERRINGTON, President, in the Chair.

THE following papers were read:—

"*The Atomic Process in Ferro-magnetic Induction.*" By Sir ALFRED EWING, K.C.B., F.R.S.

The author refers to his paper published by the Royal Society in 1890, which modified Weber's theory of the magnetisation of ferro-magnetic substances by showing that the control exerted on each elementary magnet by its neighbours was competent to explain the phenomena of susceptibility and hysteresis. In the present paper this theory is reconsidered in the light of (1) modern views regarding the structure of the atom, and (2) the X-ray analysis of crystal structure by Sir W. H. and Prof. W. L. Bragg. From the results of that analysis it appears that the rotatable Weber magnet is an attribute of the atom, not of the chemical molecule. It is not the atom itself, but probably an electron system within the atom. Metallic iron is now known to be an aggregate of crystals in each of which the space-lattice is the centred cube, with its atoms most closely grouped along the triagonal axes. It is along these axes that the Weber elements will point. Consequently an iron crystal is not magnetically isotropic.

An important characteristic of the magnetising process in iron is that there is a small quasi-elastic or reversible part preceding the much larger changes which involve hysterisis. This corresponds to a reversible deflection of the Weber magnets through a small angle, generally of an order of 1° or less. The theory of the equilibrium of a row of magnets is considered, and experiments are described in which rows of Robison magnets with ball ends have their equilibrium upset by an extraneous field. The results of these experiments confirm the theory. From the known value of the magnetism of saturation, the moment of a single Weber element is estimated, and the field is calculated which would break up rows of magnets, set in the space-lattice close enough together to bring the reversible deflection within the above limit. The field so calculated is far larger than the field that suffices to produce strong magnetisation in iron, which suggests that the ordinary laws of force between magnetic elements cease to apply at interatomic distances.

"*The Magnetic Spectrum of the β-Rays excited by the γ-Rays.*" By C. D. ELLIS.

The magnetic spectra of the β-rays ejected from various elements by the γ-rays of radium B have been examined by the focussing method used by Rutherford and others. The positions of three strong lines occurring in the magnetic spectrum of radium B are found to depend on the metal target used. Assuming that each of these three lines is due to a definite γ-radiation, it is shown, for all the elements examined, that the energy of the β-rays forming a line is equal to an energy characteristic of the γ-radiation minus the work necessary to remove an electron from the K ring of the atom. By application of the quantum theory the frequency of the γ-rays can be determined from these characteristic energies. The natural β-ray spectrum of radium B can be explained in this way, the stronger lines resulting from the conversion of the γ-rays in the K ring, and the weaker lines from a similar conversion of the same γ-rays in the L ring.

"*The Spectra of the Alkaline Earth Fluorides and their Relation to each other.*" By S. DATTA.

The present paper gives an account of an investigation undertaken to determine possible relations among the band spectra of similar compounds of different elements. Previous work by other observers suggested the alkaline earth fluorides as a suitable group of compounds for this purpose. A more complete survey of the spectra of these compounds has been made and several new bands observed. These helped in the identification of homologous series of bands in the different spectra and have suggested an empirical relation amongst them, based on the constants of the series equations and the molecular weight or the molecular number of the respective compounds.

Starting with the series equation of the band heads, a probable explanation has been given of the appearance of a "tail" in some of the bands. It has further been shown that the frequency of the tail is either a maximum or minimum, and that the difference in wave numbers of the heads and tails of the similar series is constant for the same compound, but varies from one another in a definite way.

*"A Simple Apparatus for Approximate Harmonic Analysis and for Periodicity Measurements."* By W. L. BALLS, Sc.D.

An account is given of a simple and inexpensive means for constructing and using an apparatus by which periodicities can be determined, harmonic analysis effected, and curves smoothed.

The results obtained (both with respect to length and to amplitude) are only approximately correct, but the error involved need not exceed three per cent.

The outstanding advantage of the apparatus is the speed with which determinations can be made Thus, in the case of determinations of periodicity, some fifty trial periods can be examined in less time than is required for the computation of a single trial period under the periodogram arithmetical method.

*"The Influence of Satellites upon the Form of Saturn's Ring."* By G. R. GOLDSBROUGH, D.Sc

Following upon the well-known results obtained by Maxwell that the only form of ring about a planet consistent with stability must be one made up of particles sufficiently small, this paper examines the perturbing effect of a satellite upon such a ring.

The ring is supposed to be made up of small particles—not necessarily equal—arranged in concentric circles and rotating about the primary. The satellite is assumed to follow an unperturbed circular orbit, and as a sufficient approximation, the influence of the rings upon one another is assumed negligible.

It is then shown that to a close degree of numerical approximation the satellite Mimas is responsible for the position and width of Cassini's Division and for the clean-cut termination of the whole ring. Satellite Rhea accounts for the clean-cut commencement of the inner ring (or Ring B), while a probable explanation is offered of the existence of the Crêpe Ring.

The numerical values obtained are as follows :—

| | Calculated | Observed |
|---|---|---|
| Commencement of Crêpe Ring | 9·34″ | 10 83″ |
| ,, Inner Ring | 13·07″ | 13·21″ |
| Dimensions of Cassini's Division | 16·9″ | 16·87″ |
| ,, ,, Assumed | 17·64″ | 17 64″ |
| Termination of Ring ... | 20·2″ | 20·01″ |

If $m$ be the mass of any particle, and M the mass of Saturn, and $n$ the number of particles in any single ring, then it is shown that :—

$$O < \frac{m}{M} < \frac{1 \cdot 8}{n^3}.$$

The maximum mass of a particle is thus just below the limit given by Maxwell. The inclusion of the mutual influence of the rings and the effect of the oblateness of Saturn would probably improve the agreement of theory and observation.

*"Certain Geological Effects of the Cooling of the Earth."* By H. JEFFREYS, D.Sc.

The paper deals with certain mechanical consequences of the cooling of the earth from its formation to its present state. The former fluidity of the earth is assumed for reasons given, and the information provided by radioactivity is utilised. It is found that the thermal contraction available for mountain-building is of the same order as that required to account for existing mountains. The Pacific type of mountain range can apparently be explained as a consequence of the greater cooling and consequently greater strength of the rocks below the ocean. Isostatic compensation of surface inequalities is considered due to variation in the thickness of the light rocks constituting the crust, combined with plastic flow below. On these lines the main phenomena of isostasy can be accounted for. The fact that oceans have extensive regions of less depth in the middle is explained on this theory. Theories of the formation of continents and geosynclines are suggested.

*"The Moving Striations in a Neon Tube."* By T. KIKUCHI.

## PHYSICAL SOCIETY.

*May* 13, 1921.

SIR WILLIAM BRAGG, F R.S., President, in the Chair.

THE following papers were read :—

*"Notes on Vacuum Tubes used as Detectors of Electrical Oscillations."* By Messrs. HARTSHORN and E. S. KEEPING.

I. The paper describes the development of a robust form of vacuum tube which was used as a detector of electrical oscillations in the "wireless" circuits carried by aeroplanes. Platinum electrodes are avoided, being replaced by strips of tinfoil, to which contact may be made by the spring clips holding the tube in position.

II. It was found that when a discharge is passed through such a tube, the walls are affected in such a way that thenceforth it is much easier to get a discharge to pass. The change produced by the first discharge is annulled by heating the tube above 210° C. Further, if the walls are coated on the inside with a metallic film, this first discharge is unnecessary, and the tube is unaffected by heating, but when the walls are coated with an insulator it is if anything more difficult to pass a discharge. A silica tube behaves like one coated with metal. It seems possible that the change in the tube may be due to the formation of a layer of gas molecules on the walls by the first discharge. The explanation of the behaviour of the silica tube is a difficulty.

DISCUSSION.

Prof G. W. O. HOWE mentioned that comparisons of vacuum tube detectors both with internal and external electrodes were carried out at the Reichsanstalt. Helium at various pressures was employed. Certain pressures were used to obtain extreme sensitiveness, while others were used if extreme brightness was desired. In some of the tubes issued internal electrodes were fitted, not for actual use, but for the initial preparation of the tube by electrolytic deposition of potassium on the walls.

Dr. VINCENT hoped the authors would not cease work on this interesting problem with the publication of the present paper. They had dealt only with one aspect so far, but there were a number of interesting researches, particularly in connection with valve-maintained circuits, which would suggest themselves. Mr. Hartshorn had mentioned the advantage possessed by the method that

it responded without lag during quick tuning. Another advantage was that there was no rectification of the current.

Mr. G. D. West asked if many of the authors' results in connection with the initial hardness of the tubes and the permanent softening effect of an initial discharge could not be accounted for by minute perforations of the walls by the discharge? The effects of subsequent heating appeared to fit in with this hypothesis.

Mr. W. R. Cooper asked whether the authors had looked up the work of Claude on neon tubes. These were large tubes for illumination, and it was found that a tube 6 metres long required less than 800 volts. Possibly some of the effects observed by the authors (*e.g.*, on heating the tubes), were due to the fact that the slightest impurity produced a marked effect. Claude found that it was not sufficient to use pure neon; he therefore purified the neon when in the tube itself by connecting the tube to a receiver containing carbon and immersed in liquid air.

Dr. Borns asked if a film of moisture might give rise to any of the effects?

A Visitor said that a common form of indicator in use for tuning purposes was an ordinary flash-lamp bulb. What were the conditions necessitating the use of vacuum tubes? He noticed that when responding to spark discharge it was difficult to note the brightest point on account of the intermittence of the light. This flicker is absent with a flash-lamp. The response of such bulbs was also quite quick enough for all ordinary conditions. Would a fluorescent screen in the tube increase its efficiency? What was the effect of the frequency of the oscillations on the voltage necessary for discharge?

Mr. Hartshorn, in reply, said he was not familiar with all the early work which had been mentioned. They had assumed that the experts who had referred the problem to them were aware of all that had been done on it. He did not think perforations would explain the softening of the tubes, as this would not fit in with the behaviour of some of the compound tubes. As regards moisture, the greatest care was always taken to exclude this. As regards the use of vacuum tubes it was essential that the signals should be easily seen on an aeroplane, and flash-lamp bulbs required more careful watching. As regards the intermittence, this was certainly a drawback, but was only present with spark discharges. It was not there with valve circuits. A fluorescent screen would make the tubes much too difficult to construct. Something very simple and robust was required. He did not know the effect of frequency on the discharge voltage. The figure he gave, 260 volts, was at ordinary supply frequency.

"*The Coefficient of Diffusion of certain Saturated Solutions.*" By Mr. B. W. Clack, M.Sc.

This paper gives an account of experiments on the Diffusivity of saturated solutions of KCl, NaCl and $KNO^3$ at constant temperatures near 18° C., when the steady state of diffusion has been attained, employing a method similar to that previously used by the author (*Proc. Phys. Soc.*, 1908, xxi., 863; 1911, xxiv., 40; 1914, xxvii., 56; 1916, xxix, 49).

The solution under investigation is maintained at complete saturation by the presence of salt crystals in the diffusion vessel, the theory takes into account the change in volume of this salt as it dissolves, and an expression is obtained for the coefficient of diffusion at complete saturation, which depends on the rate of change in weight of the diffusion vessel with time. The experimental results are found to agree very closely with the values obtained by extrapolation from the results previously found for less concentrated solutions. By the present paper the author has thus extended the range of concentration over which he has studied diffusion from very dilute solutions right up to complete saturation.

Discussion.

Dr. A. Griffiths dealt with the fundamental expression for diffusion. He explained the theoretical foundation of the diffusion-equation used by Mr. Clack and himself, and stated that this equation was an extension of Fick's Equation, or that Ficks' Equation could be considered to be a limiting case of their equation. He said that Fick's Equation implicitly assumes that the liquid is at rest during a diffusion operation, whereas in fact the changes in concentration in all experiments known to himself inevitably produce movement of the liquid. An extension of Fick's hypothesis is, therefore, inevitable. He explained that the equation used by Clack and himself assumed that in addition to the diffusion as expressed by Ficks, there is a movement of the diffusing salt equal in value to that of the water-component of the salt solution. He stated that the quantity defined by $\delta$ in earlier papers by Clack and himself should have been defined as the ratio of the *mass* of water entering the diffusing cell to the mass of water leaving the cell. The modification of the definition makes no change whatever when a linear relation may be assumed between density and concentration; and, in any case, makes a change smaller than errors of experiment. The change becomes smaller with the concentration, and is zero at infinite dilution.

The coefficients of diffusion for the weakest solutions of potassium and of sodium chloride were each 16 per cent less than the theoretical values given by the Nernst-equation for infinitely dilute solutions. The value of the coefficient for potassium nitrate was 11 per cent less than the theoretical. These differences could not be considered very remarkable if it were remembered that Perrin's value (based on work with liquids) for the electronic charge was 11 per cent less than the generally accepted value. The fundamental hypothesis for liquids probably require a close examination. One of his students had interpreted Mr. Clack's results by the equation $K=K_1+K_2(1-r)$, where $K$ is the coefficient obtained by Mr. Clack, $K_1$ is is the coefficient of diffusion of the completely ionised salt, $K_2$ is the coefficient of diffusion of the non-ionised salt, and $r$ is the ionisation ratio. In the case of potassium nitrate this equation represents the results obtained by Mr. Clack wonderfully well over the whole range of concentration, and it represents the results well in the case of potassium chloride and of sodium chloride when the concentrations are not great.

Capt C. W. Hume did not think the concentration at the top of the diffusion tube would be zero. The effect of this error would be equivalent to a constant increase in the length of the tube.

Mr. F. E. Smith asked if experiments could not be made by measuring differences in electrical conductivity. Such methods, it appeared to him, would enable results to be obtained much more rapidly.

Mr. Clack, in reply, said that earlier in his researches he had investigated the end-correction suggested by Mr. Hume and concluded that it was negligible. As regards the conductivity method, this

had been tried, but he was at present experimenting with an optical method with which it should be possible to obtain results for all concentrations in one experiment.

"*Experiments on Thermal Transpiration Currents.*" By Dr. G. D. West.

This paper is an attempt to demonstrate the actual existence of thermal transpiration currents. Theoretical considerations are first introduced to show that if a radial temperature gradient be maintained over a disc, so that the centre is the hottest part, thermal transpiration currents sweep radially inwards over the surface of the disc, and discharge themselves more or less radially outwards in the upper regions.

To detect these currents a narrow strip of foil is used which is placed perpendicular to the disc, and to one side of the hot region. When at a considerable perpendicular distance from the disc, and when the gas pressure is sufficiently low to eliminate convection currents, the deflections of the strip of foil are always away from the hot region. When, however, the strip is placed very close to the disc, its deflections over a certain range of gas pressure are towards the hot region. These facts are explained by the tendency of the thermal transpiration currents to drag the strip with them.

The paper emphasises one of the essential differences between thermal transpiration currents and convection currents—namely, that while the latter clearly depend on gravitation, the former do not. Further emphasis is laid on the differences between the conditions of molar and molecular equilibrium.

Discussion.

Dr. D. Owen said the author appeared to be working down to pressures of a ten-thousandth of a centimeter of mercury. How were these pressures measured?

Dr. West: With a McLeod gauge

Dr. Owen then asked if the author considered these to be reliable at such low pressures?

Dr. West replied that he always used two gauges and they gave similar results. The bulbs were from 200 c.c. to 300 c.c. capacity. He thought if care was taken to use perfectly dry air the gauges were quite reliable.

## BOOKS RECEIVED.

"A Text-Book of Assaying for the Use of Those Connected with Mines." By C. and J. J. Beringer. Revised by H. R. Beringer. Fifteenth Edition revised. Pp. xvi.+471. London: Charles Griffin & Co., Ltd. Price 12s. 6d. net.

"Reports on the Progress of Applied Chemistry." Issued by the Society of Chemical Industry. Vol. V., 1920. Pp. 625. Price to Members, 8s. 3d.; Non-Members, 15s. London: Society of Chemical Industry, Central House, 46/47, Finsbury Square, E.C.2.

"Thermodynamics and Chemistry." By F. H. MacDougall. Pp. 390. London: Chapman & Hall, Ltd. New York: John Wiley & Sons. Price 30s. net.

*Monographs of Inorganic and Physical Chemistry,*
"The Electronic Conception of Valance and the Constitution of Benzene." By Harry Shipley Fry. Pp. 300. London: Longmans, Green & Co. Price 16s. net.

"The Measurement of Study and Fluctuating Temperatures." By R. Royds. Pp. 162. London: Constable & Co. Ltd. Price 16s. net.

"Heat Transmission by Radiation, Conduction and Convection." By R. Royds. Pp. 238. London: Constable & Co. Ltd. Price 24s. net.

"Heat Transmission in Boilers, Condensers and Evaporators." By R. Royds. Pp. 302. London: Constable & Co. Ltd. Price 24s. net.

## NOTES.

The unhappy stoppage of our fuel supplies has given great impetus to the development of oil heating appliances as a substitute for solid and gaseous fuel. We are pleased to note that many useful oil heaters have been devised. The Kilson Empire Lighting Co. of Stamford, Lincs, are manufacturing heaters for linotype machines and similar purposes; judging from their drawings the burners appear to be simple and effective. It is quite possible that this information may be of use to some of our readers who may be inconvenienced by the present restrictions in other kinds of fuel.

Messrs Siemens Bros. & Co. Ltd., have sent us their new catalogue of primary cells and batteries. The firm has devoted much time and attention to the development of a serviceable dry cell, and having recently had an opportunity of testing these we can unhesitatingly recommend them for low resistance and durability.

Australian Gem Trade With France.—Acting upon the advice of the French Mission which visited Australia in 1919, the New South Wales Government sent an expert to France to investigate the possibilities of trade in Australian precious stones. On his recent return to Sydney, states the *Industrial Australian and Mining Journal*, the expert expressed confidence that an important business between France and Australia will be done in the future. France, he asserted, is keen on securing the trade previously held by Germany. Agents previously bought the precious stones on Australian diamond fields and shipped them to Germany, where they were cut and polished and distributed throughout the world. France is now in a position to take Germany's place, for she has made great strides in the gem-cutting industry, and the work being turned out is decidedly superior to that executed by German gem-cutters. Australian gems, stated the expert, received a great advertisement in the Lyons Fair, his collection exciting general admiration on account of the rare quality, variety, and distinctive characteristics of the stones exhibited.—*Board of Trade Journal.*

Iron and Steel Institute.—The Autumn Meeting of the Iron and Steel Institute will be held, by invitation of the Comité des Forges de France, in Paris, on Monday and Tuesday, September 5 and 6, 1921. At the conclusion of the meeting in Paris, alternative visits have been arranged to works in Lorraine and in Normandy, and a party of the members have been invited to visit the Creusot Works of M.M. Schneider & Co. In order that proper arrangements may be made, it is necessary that the number likely to take part in the meeting should be ascertained before June 30.—G. C. Lloyd, Secretary, 28, Victoria Street, S.W.

Egypt: Tenders Invited for General Stores.—His Majesty's Commercial Agent at Cairo, Mr. E. Homan Mulock, has forwarded to the Department of Overseas Trade copies of the specification and conditions of tender relating to the supply of general stores, to the Egyptian Ports and Light-houses Administration for the second half of the financial year 1921-1922. Tenders will be received by the Director-General of Ports and Light-houses Administration, Alexandria, up to noon on June 13, 1921. The tenderer must be a person residing in Egypt or must have a representative in Egypt. In view of this condition United Kingdom firms who are not represented in Egypt may care to avail themselves of the services of a firm with an Egyptian branch through which tenders could be submitted. Names of suitable firms will be supplied on application to the Department of Overseas Trade. A copy of the specification and conditions of tender relating to this contract may be inspected by United Kingdom firms interested on application to the Enquiry Room, Department of Overseas Trade, 35, Old Queen Street, S.W.1. A limited number of copies are also available for loan to firms in the Provinces who are unable to arrange for their inspection in London. Applications for these should bear the reference number 5054/F.E./P.N.

Postponement of Prof. Einstein's Lecture.—Owing to the postponement of the sailing of the *Celtic*, on which he had booked his passage from America, Prof. Einstein is unable to lecture at King's College until Monday, June 13, at 5.15 p.m. All the tickets which have been issued for June 9 will be available for that date.

Displacement of Metals in Saline Solutions.—Existing in an aqueous solution of one of its salts, in form of ions, a metal gives place to any more electro-negative-element than itself, or according to Nernst, of a sufficiently great dissolution tension with regard to the metal. Such is the case with copper displaced by zinc, and M. Barlot studied this phenomenon working with a thin homogeneous liquid layer. Thus arborisations are produced in form of a fan, "metallic spectra" in formation of which it seems that electric forces play a very important rôle.—*Comptes Rendus*, February 14, 1921.

Visit of the Commercial Secretary to H.M. Embassy at Athens.—Mr. E. C. D. Rawlins, Commercial Secretary to H.M. Legation at Athens has arrived in this country on a short official visit. He will be pleased to meet manufacturers and merchants who wish to discuss with him questions relating to trade with Greece, and who may desire information or advice regarding the appointment of agents, marketing and distributing goods, terms of payment, Customs duties, or general information as to openings existing for British goods Applications to interview Mr. Rawlins in London between May 26 and June 3 should be made immediately to the Department of Overseas Trade, 35, Old Queen Street, S.W.1., the reference number 3057 T.G. being quoted. It is intended that Mr. Rawlins shall subsequently visit a number of provincial centres.

Congealing Point of Mineral Oils.—According to E. Lantos, mineral oils containing paraffin in solution do not comply with ordinary cryoscopic rules In the oil industry the true point of congelation is not determined, but the solidification point, *viz.*, the temperature at which an oil, in a tube cooled with a mixture of snow and a solution of soda, and then turned with the opening downwards, does not change its meniscus during 30 seconds. In general, the slighter the viscosity, the lower the point of solidification. However, in refining two Roumanian oils it was found that although viscosity decreased, the point of solidification increased, from $-20°$ C. to $-15°·5$ C.). Galicia oils (Limanowa) containing paraffin oil had high solidification points. For example, a refined oil, rich in paraffin, with a viscosity of 2·29 had a solidification point at $+10°$ C. When the paraffin is extracted, the viscosity falls to 1·85 and solidification to $-20°$ C. These results lead to the conclusion that solutions in which the solvent and dissolved body are homologues do not comply with cryoscopic laws.—*Matières Grasses*, February 15, 1921.

Practical Methods Employed in the Stearine Industry.—The following observations are taken from a series of articles by Knor in the *Seifensie der Zeitung*. The oils and fats utilised in stearinery are kept in well-ventilated buildings with blue glass windows. They are purified by washing with sulphuric acid ($d = 1·16$) and deodorised by blowing of compressed air after heating in a vacuum to 105° C. to eliminate water; then they are hydrolysed in an autoclave with steam at 11-12 atmospheres in presence of 3 per cent CaO, 1 to 1·5 per cent MgO, 1 per cent ZnO or 0·5per cent zinc powder, preferably a mixture of 0·5 ZnO and 0·5 Zn. Magnesia is preferable for black fats and zinc powder for fats which are not distilled. Fish oils and vegetable fats require a greater percentage of hydrolytic agents and higher pressure. When hydrolysis is complete (after 8 to 10 hours) the steam valve is opened and the mixture let rest for two hours, for separation of the glycerin water; then the two layers are extracted from the autoclave. The soap is decomposed by running the fatty acids into boiling sulphuric acid ($d = 1·16$). The normal density of the glycerin water attains 1·0325.—*Matières Grasses*, February 15, 1921.

Borax and Saltpetre.—All fertilisers containing more than 0·5 per cent of anhydrous borax has been prohibited by the United States Minister of Agriculture. Regarding this regulation, Señor B. Diaz Ossa (*Caliche*, 1920, T.1., No. 11) describes the methods to eliminate this substance from residual nitrate of soda lyes from which nitrate of potash is recovered and directly employed in agriculture as fertiliser. He criticises the sulphurous gas process or that with bisulphite of soda as also that consisting in discharge of the liquid during crystallisation before this phenomenon is terminated. He recommends employment of calcium chloride to form an insoluble stable borate during concentration of the mother waters. After separation, complete crystallisation is operated. The proportion of $CaCl_2$ should be accurately calculated so as only to precipitate boric acid; the liquid should be neutral or slightly alkaline. The writer concludes with some remarks upon analysis of saltpetre from the point of view of American requirements.—*Chimie et Industrie*, February, 1921.

Finsbury Technical College.—The Governing Body of the Finsbury Technical College announce that the entrance examination for the session 1921-22 will be held on Tuesday, September 20 next Applications for admission should be forwarded to the College not later than September 15, on forms to be obtained from the Registrar, Leonard Street, City Road, E C. The programme of the College is under revision and will be issued in due course. We are pleased to learn that the work of the Chemical Department will be continued; Mr. W. J. Hale is acting head of the Department.

Mr. Henry Mayer, the Chairman of Henry Mayer & Co., Ltd., has left the Pottery and Glass Trades' Benevolent Institution the sum of £500 to be used as an endowment in perpetuity, and the income applied towards providing an annuity or annuities for the widow or widows of members. The endowment to be known as the Henry Mayer Bequest.

Principles of Analysis by Means of Reductive Flames; Research for Traces of Manganese in Presence of Iron or Other Substances.—Continuing the application of the method he gave in 1914 (Congress of the French Association for the Promotion of Science), which consists in conveying away a solid salt or oxide in a flame of hydrogen and photographing the spectra of the rays obtained by aid of an ingenious technique, M. I. Meunier applied this method to analysis of iron, thus being able to follow the elimination of manganese by the disappearance of the triplet of this metal. The method is very sensitive with pulverulent oxides or oxalates.—*Comptes Rendus*, March 14, 1921.

We have received from the Royal Insurance Co. Ltd., their eighth edition of the "Rules of Golf," as amended on September 28, 1920. It is issued in a practical and concise form, containing a comprehensive index. The Company has also issued with the above edition a small leaflet, showing the differences between the old and new Rules, and especially relating to the new standard of ball, which we are sure will be appreciated by all followers of the "Royal and Ancient Game."

Visit of the Commercial Secretary to H.M. Embassy at Madrid.—Captain U. de B. Charles, Commercial Secretary to H.M. Embassy at Madrid, has arrived in this country on a short official visit, and will be pleased to meet manufacturers and merchants who wish to consult him in regard to steps to be taken for opening up trade with Spain, and who desire information as to the state of trade in that country. Among the matters in regard to which he will be prepared to give advice and information are the appointment of agents, methods and marketing and distributing goods, terms of payment, statistics of imports, rates of Customs duties, and general information as to openings existing for British goods. Firms desirous of making appointments to interview Captain Charles in London from May 24 to June 3 should communicate immediately with the Department of Overseas Trade, 35, Old Queen St., London, S.W.1., quoting the reference 3055 T.G If circumstances permit, it is intended to make arrangements for Captain Charles to visit other centres in the United Kingdom after June 3.

## New Patents.

This List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W C 2, from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

13664—Adam, W. G—Manufacture of amines from phenolic compounds. May 13th.
13180—District Chemical Co., Ltd.—Materials for purifying acetylene gas May 9th
13210—Gaillard, E. A.—Manufacture of sulphuric acid. May 10th.
13675—Hoffman-La Roche & Co., Akt. Ges., F.—Process for manufacture of 1-alley 1-3. 7-dimethylxanthine. May 13th.
13656—Oehlrich, F J. G.—Process for production of a contact mass for catalytic synthesis of ammonia. May 13th
13261—Wilton, N.—Manufacture of sulphate of ammonia. May 10th.

*Specifications published this Week*

140051—Sasa, H.—Manufacture of phthalic anhydride.
145781—Collin Akt Ges. zur Verwertung von Brennstoffen und Mettalen, F G.—Method of discharging ammonium sulphate from saturrater baths.

*Abstract Published this Week*

*Naphthylene-diamine Derivatives.*—Mr. G T. Morgan of the Imperial Trust, 15, George Street, Westminster, has been granted a Patent No 160853 for improvements in the preparation of arylsulphonyl or arylenedisulphonyl derivatives of sc-naphthylenediamine or its sulphonic acids, by reducing the p-azo derivatives of arylsulphonyl-bis-sc-naphthylamines or their sulphonic acids containing the sulphonic radicle in the 2, 6, 7 or 8 position with respect to the arylenedisulphonylamino radicle. According to the provisional Specification, these bodies may also be prepared by reduction of the corresponding p-nitro compounds. The following reducing agents are mentioned as suitable · zinc dust and caustic soda, zinc dust and ammonium, chloride, iron borings and dilute acids, alkaline sodium sulphide, stannous chloride and titanous chloride. The p-azo derivatives above-mentioned are produced by condensing x-napthylamine or its sulphonic acids in the positions specified with arylsulphonic acid chlorides or arylenedisulphonic acid chlorides and causing the resulting compounds to react with diazonium compounds in alkaline media. Examples are given to the preparation of toluene-p-sulphony 1-1 : 4 naphthylenediamine and its 8-sulphonic acid, benzene 1: 3-disulphonyl-bis-1 4-naphthylenediamine and its 8-sulphonic acid, and naphthalene-2 : 6-disulphonyl-bis-1 . 4-naphthalenediamine.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

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## NEW COMPANIES.

The under-mentioned particulars of New Companies recently registered are taken from the Daily Register compiled by Jordan & Sons, Limited, Company Registration Agents, Chancery Lane, W.C.2.

W. H S. Clark & Co., Limited.—(174721)—Registered 13th May, 1921. 56, High Street, Lewes, Sussex To carry on the business of Manufacturers and Dealers in Manures and Fertilizers of all kinds and Dealers and Merchants of Farm and other Produce. Nominal Capital · £6,000 in 120 Shares of £50 each. Minimum Subscription · 20 Shares. Directors. W. H. S. Clark, 80, St. Helens Road, Hastings; H. J. Chapman, Ivy Bank, Sutton Park Road, Seaford; W. A. Cowley, Woodingdean, Rottingdean, Near Brighton, F. Martin, Wasbourne, Sheffield Park Street, Lewes; A. Leggat, Mill Place Farm, East Grinstead; G. Hemsley, Boat House Farm, Isfield, Sussex. Qualification of Directors: 2 Shares. Remuneration of Directors: £25 each.

Devon Chemical Company, Limited.—(174769)—Registered 19th May, 1921. Harlington, Newton Abbot, Devon. To carry on the business of Chemists and Druggists. Nominal Capital: £500 in 500 Shares of £1 each. Directors. G. F. Storey, 15, Ashleigh Road, West Park, Leeds; N. V. Stow, Harlington, Newton Abbot, Devon; A. W. Simpson, H tfield, Bonnybridge; J H. Keighley, 63, Argyle Street, Keighley; H. S. Prince, 22, Victoria Terrace, Leeds. Qualification of Directors · 1 Share. Remuneration of Directors: To be voted by Company

Zeta Drug Company, Limited.—(174787)—Registered 20th May, 1921. 180, Fleet Street, E.C.4. To carry on the business of

Chemists and Druggists Nominal Capital £500 in 500 Ordinary Shares of £1 each. Directors: T. C. King, 15, Aldersgate Street, E C.; S. Westall, 37, Upper Berkeley Street, W.1. Qualification of Directors: £100 Remuneration of Directors. To be voted by Company in General Meeting

MABYN & COMPANY, LIMITED.—(174800)—Registered 20th May, 1921. To carry on the business of Manufacturing, Wholesale and Retail Chemists and Druggists Nominal Capital. £500 in 500 Shares of £1 each. Directors: H.W. W. Northwood, 1, King David Lane, E 1., (Governing Director and Chairman). Qualification of Directors: 1 Share.

*Private Companies.*

SLAG PHOSPHATE COMPANY, LIMITED —(174808)—Registered 20th May, 1921. To carry on the business of Manufacturers and Dealers in Slag Phosphates. Nominal Capital: £250,000 in 250,000 Shares of £1 each. Directors: Sir J. R. Wright, Bart, Widcombe Manor, Bath, Sir W. C. Wright, K.B E., 31, Princes Gate, W F. W. Gilbertson, Langland Bay, Swansea; J C. Davies C B.E, The Mount, Gowerton, G. V. Parker, Skelmorlie, Newport Qualification of Directors 5,000 Shares. Remuneration of Directors: To be voted by Company.

## MEETINGS FOR THE WEEK

*Monday, June 6.*

Royal Institution, 5. (General Meeting).

*Tuesday, June 7.*

Royal Institution, 3. "London Life" by Sir James Frazer.
Röntgen Society, 8.15.

*Wednesday, June 8.*

Institution of Electrical Engineers, 5.30. (Wireless Section). "Electric Oscillations along Straight Wires and Solenoids" by Prof. J. S. Townsend.

*Thursday, June 9.*

Royal Institution, 3. "Beethoven" by Sir Alexander C. Mackenzie.
Institute of Chemistry (At Liverpool).
Optical Society, 7 30.

*Friday, June 10.*

Royal Institution, 9. "Absolute Measurements of Sound" by Dr. Arthur Gordon Webster.
Physical Society, 5.

*Saturday, June 11.*

Royal Institution, 3. "Scott and Shakespeare" by Dr. Robert S. Rait.

## NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemical Apparatus, &c, for review or notice to be addressed to the EDITOR.

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THE CHEMICAL NEWS.
VOL. CXXII., No. 3191.

# THE SOIL SOLUTION IN RELATION TO THE PLANT.*

By D. R. HOAGLAND, University of California.

THE soil and plant together form a multiple phase chemical system, and a more exact knowledge of the inter-relationship of the various components of this system is requisite to the advance of scientific investigations of the soil in its relation to the plant. The fertility of any soil must be measured by its ability to produce some useful crop; thus the study of soil fertility cannot be dissociated from the study of plant growth. Perhaps these ideas may be considered too obvious to require statement, yet it is true that this point of view often fails to receive proper consideration in researches dealing with soils and plants, even when the avowed purpose is that of contributing information directly or indirectly applicable to crop production.

Innumerable analyses of soils have been made to determine the total content of plant food, or to estimate what proportion of the total quantity is soluble, under arbitrarily limited conditions, in hydrochloric acid, nitric acid, or other strong solvents, which at various times have been thought to bring into solution only the more or less available soil constituents. Notwithstanding the enormous mass of data obtained in this manner, no general and consistent correlation with crop production has ever been made. The conceptions of the soil which underlie this type of experimentation are essentially static in nature, while the plant and the soil form a dynamic system in which rates of processes are all important. In this paper the writer has for his main purpose the further elaboration of the dynamic and physical-chemical viewpoint of soils and plants, first desiring to acknowledge his indebtedness to the work of the Rothamstead Station, the Michigan Station, and others, and to the investigations of Burd and Stewart at the University of California.

Since the plant obtains its direct supply of mineral nutrients only from solution, the soil solution at once becomes the logical point of attack in investigations of plant nutrition. The difficulties met in researches in this field are manifold, and have been overcome only to a limited degree, but certain assumptions may be made with a very great measure of confidence. Whatever may be the forces by which the film water is bound to the soil particles, it must nevertheless possess many, if not all, the chemical properties of free solutions. Among these properties certain ones may become of paramount importance to the nutrition of the plant, for example, reaction, osmotic pressure, and concentration of nutrient ions. There seems to be no valid reason against the application of physical-chemical principles applying to solutions which nourish the plant.

During recent years many researches have shown that the reaction or hydrogen ion concentration of solutions is of far-reaching interest to the biologist. In the realm of soil investigations there has long existed the utmost confusion concerning the question of soil reaction. Many terms have been invented to describe a varying complex of factors, such as "sour soil," "apparent acidity," "so-called acidity," "adsorption acidity," "negative acidity," &c. Numerous investigators have been loathe to acknowledge that a soil solution could be acid in the same sense as any other acid solution. But we must of necessity recognise the fact that the soil solution is either acid, neutral, or alkaline. The investigations of the past few few years with the hydrogen electrode and special indicators seem to leave no doubt that many soils yield solutions with hydrogen ion concentrations greater than that of pure water. Such solutions are properly termed acid, and the term requires no modification.

Upon examining into the intensity of acidity (most conveniently represented by the customary *p*H values) of such solutions, we find that there is no evidence to prove that the acidity *per se* is sufficient to be injurious to most plants of agricultural interest, except in somewhat rare instances. This conclusion is upheld by experiments with solution cultures, which prove that plants may grow normally in solutions having intensities of acidity comparable with those found in most acid soils (D. R. Hoagland, 1918; *Science*, N.S., xlviii., 1-8; *Ibid.*, 1919; *Jour. Agr. Res.*, xviii., 73-117). Further confirmation is afforded by observations on certain peat soils of California. In these soils many crops, including legumes, thrive and yet the acidity is of the order of *p*H 4, 8. The so-called lime requirement of the soils is enormous, but the addition of lime has not resulted in increased crop yields.

It is, of course, undeniable that the practice of liming acid soils is most frequently beneficial to the plant, but it by no means follows that the improved environment is directly attributable to a decrease in the hydrogen ion concentration of soil solution. It has been shown that aluminum in toxic concentrations may be present in some acid soils; the decrease of acidity may be accompanied by a decreased concentration of aluminum. In other cases the base-silicate equilibrium may be of such a nature as to prevent the attainment of a concentration of calcium sufficiently great for the needs of some plants; the addition of lime may alter this system and remedy the deficiency. Many other possibilities could be suggested, including speculations concerning the effect of reaction on soil micro-organisms. Those interested only in the art of agriculture may object that it is immaterial what the mechanism may be, by which an acid soil is improved by the use of lime, but the scientfic investigator will desire to segregate out the diverse factors of the complex system and assign to each one its due weight. In no other way can the true relation between soil reaction and plant growth be ascertained.

Brief mention should be made of soils with alkaline soil solutions. Here also elementary physical chemical principles assist in the interpretation of the data. Soils containing calcium carbonate are usually referred to as alkaline soils, and it is very generally maintained that most plants, especially leguminous plants, require an alkaline medium. A more careful consideration of the chemical

*A Contribution to a General Discussion on "Physico-Chemical Problems Relating to the Soil" held by The Faraday Society, on Tuesday, May 31, 1921.

equilibria leads to the inference that the soil solution of a soil containing calcium carbonate is not necessarily always appreciably alkaline in reaction In such a system one must take into account the partial pressure of carbon dioxide in the gaseous phase of the system. It has been well established by the work of Russell and others (E. J. Russell and Alfred Appleyard, *Jour. Agr. Sci.,* 1915, vii., 1-48) that the soil atmosphere may contain much larger percentages of carbon dioxide than the outer atmosphere. The real reaction of the soil solution will be dependent in part on the partial pressure of carbon dioxide. If this partial pressure be sufficiently great a nearly neutral or possibly slightly acid reaction will be found in such soil solutions. The hydrogen ion concentration would be subject to continuous modification with fluctuations in the carbon dioxide content of the soil atmosphere. Since the plant at certain periods may bring about a large increase of carbon dioxide in this atmosphere, it is evident that the plant may exert an appreciable effect on soil reaction in soils of this character. The soil micro-organisms have a like significance in this connection.

In arid regions soils are often found in which the reaction is determined by a sodium carbonate, bicarbonate, silicate system. Under these circumstances an excessive hydroxyl ion concentration may sometimes exist, the intensity of alkalinity being sufficiently great to destroy most useful plants. In general, for a similar divergence from the neutral point, within a limited range, the hydroxyl ion seems to be more toxic than the hydrogen ion. In these soil systems also carbon dioxide is an essential factor, and its presence tends to decrease the actual alkalinity of the solution. Recent work has indicated that it is impossible to understand the effects of such soils on plants unless this factor be given consideration.

While the reaction, or hydrogen ion concentration of the soil solution is of extreme interest in many special cases, the concentration of the nutrient ions is of universal significance to soil fertility investigations. Two great obstacles have hindered progress in this field; first, the difficulty of separating the soil solution from the soil mass, and second, the fluctuating nature of the solution. Lipman (Chas. B. Lipman, *Univ. of Calif. Pub. Agr. Sci.,* 1918, iii., 131-34) and others have attempted to obtain the soil solution with the use of great pressure, but definite conclusions have not been formulated at the present time. The approximate magnitudes of total concentration of solutes in the soil solution have been determined by Bouyoucos and McCool (G. J. Bouyoucos and M. M. McCool, *Mich. Agr. Exp. Sta. Tech. Bull.*, 24, 1916, pp. 592-631) by means of an application of the method of freezing-point depression. Some of the results secured with the aid of this procedure have thrown considerable light on the whole question, although it is not at all certain that the small differences in depressions of the freezing-point noted in some investigations do not fall within the limits of experimental error. Observations from freezing-point determination indicate that the fertile soils examined had, at optimum moisture content, solutions of concentrations represented by from 0·05° C. to 15° C. freezing-point depression, when the concentrations were at the maximum. After the depletion of the solution by the plant, the values frequently fell off to as low as 0·01° C. to 0·005° C., or even less (G. R Stewart, *Jour. Agr. Res.,* 1918, xii., 311-68).

Analyses of water extracts of soils, periodically carried out, have contributed greatly to our knowledge of the solutes available to the plant. Studies on the relations existing between the freezing-point depression and the quantity of solutes dissolved in water extracts have indicated that in general the concentration of the soil solution is reflected in the extract Still other applicable data have resulted from experiments on the equilibria between soil extracts and soil mass (D. R. Hoagland, *Jour. Agr. Res.,* 1920, xx., 381-95), and these have suggested that the ratios between some of the solutes may be similar in the soil solution and in certain types of water extracts.

Incomplete as our information is, we may still construct on the basis of our present knowledge an outline of some of the important characteristics of a soil solution, pertaining to its nutrient properties. It is very certain that soil solutions are of infinite diversity. The theory at one time advanced by Cameron, to the effect that all soil solutions were saturated with respect to important nutrients is of course untenable. Indeed, the fallacies of this conception were long ago clearly pointed out by Russell (E. J. Russell, *Jour. Agr. Sc.,* 1905, i., 327-46). It has required the recent work, however, to establish more definitely some of the relations existing between crop and season and the soil solution.

These relations can perhaps be conveniently illustrated by a brief reference to the California experiments. Large quantites of different soils were collected in one place, and after careful mixing, they were placed in containers, each of about one ton capacity. Two containers of each soil were installed, one being cropped to barley, and one remaining uncropped. Samples of the soils were taken every two weeks, and the water extracts analysed. During the early period, while the plants were still very small, an increase was noted in the quantities of nitrate, potassium, calcium, and magnesium extracted. After the plants had begun to grow more rapidly, the amounts of these elements in the extracts started to decrease, and by the time the plants were well tillered and the heading-out stage had been reached, little, if any, nitrate remained, and in general very significant depressions of soluble potassium, calcium, and magnesium had occurred. Meanwhile the uncropped soils failed to show these decreases in the water-soluble nutrients, although marked fluctuations were found, probably associated with cycles of activity of micro-organisms In these uncropped soils the highest point in the seasonal curve was frequently attained at the time when the cropped soils were at a minimum. The water-soluble constituents of the latter slowly increased in quantity after the periods of greatest depression but the difference between the cropped and uncropped soils persisted for a long time, sometimes being evident at the beginning of the following season. Later other crops than barley were experimented with, and very similar results were obtained.

The seasonal fluctuations which have just been described do not seem to hold for phosphate. The water-extractable phosphate on the whole is main-

tained at a fairly constant level throughout the season, but different soils yield very different quantities of soluble phosphate. While no marked changes are noted during a single season, after a number of years of cropping some soils show a decided depression in the solubility of phosphate. Thus we may assume that the crop does produce an effect on the concentration of phosphate ion in the soil solution, but the chemical system involved requires special consideration. The total quantity of phosphate extracted from a soil is approximately proportional to the amount of water used, which is not true of potassium, calcium, magnesium, and nitrate.

The next step in the investigation was to follow the absorption of nutrient elements by analysing the crop itself at various stages in the growth cycle. This task was undertaken by Burd (J. S. Burd, *J. Agr. Res.*, 1919, xviii., 51-72), and his experiments indicated very definitely that the absorption of certain elements was characterised by several distinct phases, coincident with important stages in the development of the plant. Up to the time of heading out the total quantities of all elements increased in the tops of the plants. At this period a new phase began, during which a loss of nitrogen and potassium from the tops (and possibly a slight loss of calcium and magnesium) occurred. Later there was a period of renewed absorption.

Perhaps this course of events might be thought to be inherent in the growth of the plant. When, however, plants are grown in solution cultures, and provision is made to maintain more or less continuously a sufficiently high concentration of the nutrient elements, absorption may continue throughout the cycle of growth. It would seem probable therefore, that both the diminution in concentration of the soil solution and changes in the internal metabolism of the plant are concerned in the phenomenon of loss of nutrient elements from the tops as a whole. These conclusions are based on experiments with barley; but there is reason to suppose that they are of more general application.

At this point in the discussion the question naturally arises, what are the characteristics of a soil solution producing maximum yields of crop? Many of the soils referred to in this paper produced very large yields of barley straw and grain. From this it must follow that the very low concentrations of the soil solution in the later stages of growth were not unfavourable to the production of a large crop. The important period of absorp- of nutrients for barley occurred before the heading-out stage. These conclusions may not be valid for phosphate, since, as has been stated, this ion is probably maintained at a more nearly constant concentration in the soil solution, and, moreover, absorption of phosphate continues, even during the period of loss of nitrogen and potassium. In an artificial culture solution the decrease in concentration occurring in soil solutions may be prevented. When this is done, and when the climatic conditions are suitable, a very large growth may be obtained from a single seed. Here a special and somewhat abnormal condition is produced, in which new cycles of growth succeed each other and great delay in ripening processes may be brought about. It also appears that plants grown under these conditions may acquire very high percentages of certain elements, notably nitrogen and potassium.

Having thus outlined some of the general relations of soil to plant, it may be well to consider for a moment the question of ratios between nutrient elements. Great importance has frequently been attached to the specific ratios between the salts used in preparing nutrient solutions. Certain definite proportions are claimed to be essential for optimum growth of a given plant. The writer feels that these claims are in no manner justified by the evidence adduced in their support. Very serious criticism may be made of the methods of experimentation and interpretation of data (D. R. Hoagland, *Jour. Agr. Res.*, 1919, xviii, 73-117). Another point of view bearing on this phase of nutrition may be gained by further reference to the soil experiments. It is obvious that terrestial plants have generally adapted themselves to growth in the soil, their natural habitat, and it is not unreasonable to draw certain deductions with regard to the nutrient requirements of the plant from data on soils which actually produce excellent crops. There is no evidence from observations of this character that the plant is under the necessity of obtaiing its nutrients from solutions with definite ratios between the solutes. On the contrary equal yields may be obtained from soils which give extracts with very different proportions between important elements. As is well known, the composition of plants with respect to ash constituents may vary greatly. Moreover, a brief inspection of the curves of seasonal fluctuations for soluble nutrients will show that the ratios between the solutes are constantly changing, since not all the elements are absorbed at equal rates, nor are they replenished in the soil solution in the same way. It is perhaps needless to state that extreme cases may occur, particularly in the so-called alkali soils, in which the balance of ions may become of importance.

What, then, constitutes adequacy in a soil solution? According to Burd (J. S. Burd, *Jour. Agr Res.*, 1918, xii., 297-309), the soil extract, even of a soil of inferior production, contains at any time a sufficient quantity of water-soluble nutrients for the needs of the plant, as judged by actual absorption of these elements by crops growing in fertile soils. This apparent anomaly is capable of explanation when we take into account several important factors which limit the interpretation of data obtained by the method of water extracion. In the first place it is to be noted that at the time of greatest depletion very little nirate remains in the soil. The analytical difficulties are of such a nature that an ovestimate of the supply of nitrate may be made when only small amounts are present. Also a large quantity of nutrients not actually present in the soil solution at a given time is dissolved from the soil mass by the excess water used in making the extracts. As already pointed out by Russell, (E. J. Russell, *Jour. Agr. Sci.*, 1905, i., 327-46), diffusion is a very important matter in this connection. Availability of nutrients should properly be measured by the rate at which these are supplied to the absorbing membranes of the root system, but experiments based on water extracts cannot determine availability in this sense with any degree of accuracy. Without doubt the colloidal nature of the soil and the type of plant must be taken into consideration.

For these and other reasons it may not be possible to correlate the analyses of water extracts of soils with differences in productivity, except when the magnitudes are fairly large, but one is perhaps justified in believing that the seasonal curves for aqueous extracts of soils from the most secure basis so far considered for interpreting the nutrient properties of the soil in terms of plant production. Information leading to a greater appreciation of the role of the soil solution must also be fundamental to any rational explanation of the effects of fertilisers on soils and plants.

Our thesis concerning the plant and soil as a chemical system brings us to the consideration of another phase of the whole question. The growth of the plant is dependent not only on the soil, but on temperature, light, and humidity—the climatic complex. It has sometimes been said that weather has more to do with crop yield than any modification which can be made in most soils. Furthermore, the climatic complex influences the soil solution directly and indirectly. The requirements of the plant probably vary with its aerial environment, and the effect of the plant on the soil solution must likewise vary. Neither can the effects of climatic conditions on the activities of micro-organisms be neglected, since biochemical processes are of paramount importance in their influence on the soil solution.

The dynamic view-point of soils and plants leads to certain very clear suggestions for future experimentation on soils. The rates of solubility carbon dioxide production, nitrification, absorption of solutes by different plants, &c., must receive much more attention, and plants must be grown under definitely controlled environments. This means that in certain experiments light, temperature, and humidity should be subject to variation at will. The difficulties of an adequate control in soil and plant experiments are immense, but the field of research which would be opened by these refinements of experimental methods is unlimited in its opportunities. By such researches we may hope to understand to a far greater degree than heretofore the complex system of chemical reactions which determine every step in plant growth.

## THE ESTIMATION OF HYPOCHLORITES AND CHLORATES BY HYDRAZINE.

By ALEXANDER KILLEN MACBETH.

De Coninck (*Compt. Rend.*, 1898, cxxvi., 1042) pointed out that hypochlorites, amongst other agents, were capable of oxidising hydrazine with the liberation of nitrogen; but although the observation was published over twenty years ago, no attempts appear to have been made to apply the gasometric method suggested by the reaction to the estimation of hypochlorites in solution. Williams (*Proc. Chem. Soc.*, 1912, xxviii, 327) employed hydrazine for such estimations, but his method was a volumetric one, the end point in the titration being determined by starch iodide paper. His values for hypochlorite present in solution, obtained by this method, agreed with the results calculated from titrations with arsenious acid, and the reaction was accordingly represented according to the equation

$$2MOCl + NH_2.NH_2 = 2MCl + N_2 + 2H_2O.$$

The gasometric method depending on the nitrogen liberated is found to give good results, and furnishes a rapid and convenient means of estimating hypochlorites. The operations are accurately and quickly carried out if a Van Slyke nitrometer (*J. Biol. Chem.*, 1912, xii., 278) is employed. Solutions of potassium hypochlorite were prepared by passing a slow stream of chlorine into a cooled aqueous solution of caustic potash, an excess of chlorine being avoided. 5 cc. of this solution were introduced into the deaminising bulb, and 7 cc. of an alkaline solution of hydrazine added. The latter is conveniently prepared by dissolving 5-10 grms. of hydrazine sulphate and 10-15 grms. of caustic potash in 100 cc. of water. Nitrogen is rapidly evolved, and after the temperature has become steady the volume of nitrogen liberated is noted. Comparison of the values obtained by this method with those determined by titrations with arsenious acid or sodium thiosulphate and iodine show that the nitrogen is evolved quantitatively according to the equation given above. For example, in one set of experiments the hydrazine estimation gave a result of 16·13 grms. of potassium hypochlorite per litre, the arsenic titration gave a figure 16·063 grms., and the thiosulphate method gave 16·11 grms. In another series the values were 23·55, 23·54, and 23·55. With more concentrated solutions a similar agreement was noted. Each cc. of nitrogen, measured at N.T.P., therefore corresponds to 0·008079 grms. KClO or 0·004687 grms. HClO.

Very good results were also obtained in estimating the available chlorine present in bleaching powder. The reaction proceeds rapidly according to the equation

$$Ca(OCl)_2 + NH_2.NH_2 = CaCl_2 + N_2 + H_2O.$$

Each cc. of nitrogen, measured at N.T.P., therefore corresponds to 0·006328 grms. of "available" chlorine. Thus, a solution of bleaching powder which required 13·0 cc. of N/10 arsenious acid for the titration of 10 cc., was found on treatment with hydrazine to liberate 15·6 cc. of nitrogen at 18°, 760 mm. from 20 cc. of solution. The former value gives 4·6 grms. of "available' chlorine per litre; the latter gives 4·63 grms. Values obtained in another series of experiments were respectively 21·9 grms. and 21·88 grms. per litre.

It is thus evident that the method is a rapid and accurate one for the estimation of hypochlorites in the absence of free chlorine. Good results are not obtained if this is present.

Hodgkinson (*J. Soc. Chem. Ind.*, 1914, xxxiii., 815) pointed out that alkali, and other, chlorates were acted upon by hydrazine salts in the presence of fragments of copper wire, copper oxide, iron and iron salts, and other catalysts. The chlorates are completely reduced, and the reaction proceeds according to the equation

$$2KClO_3 + 3NH_2.NH_2, HNO_3 = 6H_2O + 3N_2 + 3HNO_3 + 2KCl.$$

In his estimations, Hodgkinson used an excess of the hydrazine salts, and after the reduction was complete, the excess of hydrazine was destroyed by treatment with potassium permanganate and nitric acid; the chloride in solution was then determined in the usual way, and the original amount of chlorate was thus calculated. It seemed probable that the gasometric method might be conveniently applied in the estimation of chlorates, but the results we obtained were highly unsatisfactory in all cases.

## THE PURIFICATION AND SOME PHYSICAL PROPERTIES OF CERTAIN ALIPHATIC ALCOHOLS.

By ROGER F. BRUNEL, J. L. CRENSHAW and ELISE TOBIN.

(Continued from 258.)

*The Boiling-Point Apparatus.*—The apparatus finally adopted is shown in the original paper. It is 32 mm. wide in the main part, and 53 cm. high. The air jacket is preferable to an asbestos wrapping since the behaviour of the boiling liquid can be watched. The glass stopper is drawn down to a neck of 11 mm. diameter so that a small cork serves to hold the thermoelement. The same cork was used continuously so that any soluble material must soon have been extracted, and any absorbed alcohol could easily be driven out. Gold scraps were usually placed in the apparatus to facilitate boiling, but experiments without them seem to have proved them superfluous. With this apparatus about 20 cc. of alcohol sufficed for a test.

The side arm was made of tubing of 10 mm. internal diameter in order to avoid rise above atmospheric pressure with vigorous boiling. With a sufficiently narrow outlet tube such changes may occur, but this is a source of error easily avoided. The most persistent difficulty which we had to overcome was the *fall in boiling point* which always occurred with the higher boiling alcohols *when the flame was raised* and the violence of boiling increased. It was suspected that the backflow from the condenser was the cause of this, and the apparatus with the return tube for condensed liquid was therefore adopted. But this was not the cause of the trouble. The real cause was found to lie in the failure to dry the alcohol thoroughly. (The boiling-point of a perfectly pure substance can, as a matter of fact, be determined with very few precautions as regards the apparatus. We finally tested the boiling point of *n*-butyl alcohol in an apparatus consisting of a tube 33 mm. in diameter by 45 cm. high, with a side tube for condenser near the top, with no air jacket or insulation of any sort, but with shield about the thermoelement. The result was identical with that obtained with the other apparatus. It would appear that such an apparatus as that of Edwards (*C.A.*, 1918, xii., 1261), in which care is taken to have the inner chamber surrounded by a jacket of vapour at the same temperature, involved somewhat unnecessary precautions. Nevertheless, a jacket of some sort is, of course, desirable, since, otherwise, air currents interfere with careful regulation of the rate of boiling).

*Drying Agents.*—The alcohols were all originally boiled with and distilled from lime until no apparent further action occurred before fractionation was begun. The subsequent prolonged boiling during the fractionation appeared to dry them completely. When, however, the boiling points were tested, it was found necessary to repeat the drying. (See Young and Fortey, *J. Chem. Soc.*, 1903, lxxxiii., 65, in this connection. The remarks of Winkler, *Ber.*, 1905, xxxviii., 3616, regarding over emphasis which he considers has been placed on the hygroscopicity of ethyl alcohol, appear to us misleading. We find it impossible to keep our compounds dry). We at first tried to distil the small quantities needed for the tests (about 20 cc.) from a drying agent into the well-dried boiling-point apparatus, but found it impossible to get a constant boiling specimen in this way. The tests have therefore been made with the drying agent in the apparatus. A test of the boiling point in this apparatus apparently shows the presence of the least trace of moisture, at least when the alcohol boils above 100°. With a sufficiently low flame the water, in such a case, gradually accumulates in liquid condensed in the upper part of the apparatus and in the condenser, beyond the point where it can be washed down. The boiling point gradually rises to a maximum, which has proved to be very close to the true boiling point of the alcohol, provided the amount of water present is not too great. *But as soon as the rate of boiling is increased so that the walls are washed down, the temperature drops.* Such fluctuations have often amounted to 0·3°, and were always observed with alcohols boiling abve 100°.

This explanation of these fluctuations is borne out by the fact that with sufficient drying the boiling point became constant. Furthermore, in the case of several specimens of alcohols which were not boiling constantly, the apparatus was tipped and the alcohol distilled through the side arm. The first few drops of such distillates in every case turned copper sulphate blue, while water was not detected in the main portion of the distillate by the same test.

The complete drying of these specimens, presumably nearly dry at the start, was, however, so difficult that the action of drying agents was given special consideration. The matter does not appear to have been thoroughly discussed in the literature. When a metal or metallic oxide is used to dry an alcohol, the following set of equilibria must exist as soon as hydroxide is formed:

$$\begin{array}{ccc} \mathrm{MOR+HOH} & \rightleftarrows & \mathrm{MOH+HOR} \\ \downarrow\uparrow & & \downarrow\uparrow \\ \mathrm{MOR} & & \mathrm{MOH} \\ \text{solid} & & \text{solid} \end{array}$$

M being the metal, and R the alcohol radical.

The effectiveness of the drying agent will evidently depend upon (1) the equilibrium constant of the reaction in solution, which, however, should not vary greatly with different metals; (2) the solubility of MOH and MOR. The solubility of the base should obviously be as small as possible, while solubility of the alcoholate will be favourable.

In addition, the dissociation pressure of water over the hydroxide must be taken into account, although this is probably too small with any of the metals concerned to be of any consequence (see Johnston, *Jour. Amer. Chem. Soc.*, 1908, xxx., 1357).

The velocity with which a drying agent will act is a different matter. It obviously depends upon the rate of its reaction with water, but when the concentration of water becomes low so that the velocity of its reaction with the drying agent is very small, a rapid action of the drying agent

with the alcohol, forming an alcoholate which is appreciably soluble, will be as effective as direct action with the water, since the alcoholate will at once react with the water, precipitating metallic hydroxide.

*Sodium*, in view of the above considerations, could not be expected to be an effective drying agent, by reason of the high solubility of the hydroxide. The addition of sodium to a specimen of *n*-butyl alcohol in the boiling point apparatus proved to be quite without effect. The fluctuation of the boiling point was the same after its addition as before, while the maximum temperature attained with a low flame was 0·015° below the true boiling point.

Lime should be much more effective. Lassar-Cohn (Lassar-Cohn, "Arbeitsmethoden," 1906, i., 265), quotes Smith (Smith, *Arch Pharm.*, 1876, p. 356) as having shown that 50 cc of alcohol in contact with lime contains only 0·0005 g. of solid. Since the hydroxide is probably less soluble than the alcoholate, the equilibrium must be driven far to the right, so that the alcohol is practically dry.

The amount of water which could remain in such a solution, in the presence of lime is, moreover, limited to the amount which would have a vapour pressure equal to the dissociation pressure of water over calcium hydroxide at the temperature concerned. At the boiling point of butyl alcohol, with which we have tested this question, 117°, this pressure would be, according to Johnston's (*loc. cit.*) equation, 0·00002 mm. It would appear that such alcohol could reasonably be called dry.

Mendelejeff (*Z. Chem.*, 1865, p. 261) nevertheless claimed that alcohol could take water from calcium hydroxide, and when difficulty was met with in drying the alcohols completely with lime the matter was tested by addition of calcium hydroxide to thoroughly dried butyl alcohol. In the two most conclusive experiments *n*-butyl alcohol was first dried with aluminum amalgam until it boiled constantly at 117·705° and 117·707° respectively. The first specimen slightly hydrated lime, to the second freshly slaked lime dried by brief heating to 200° was added. In neither case was the boiling point altered by 1 $\mu$v., even after further standing and boiling.

*Calcium* acts more rapidly than lime, largely because of the rapid formation of the alcoholate. In the only case in which we used it, however, a constant boiling point was not obtained, and since both Osborne, McKelvy, and Bearce (*Jour. Wash Acad. Sci.*, 1912, ii., 95), and Robertson and Acree (*Amer. Chem. J.*, 1913, xlix., 494) found that ethyl alcohol had a higher density when dried with calcium than when dried with lime, it appears possible that the calcium usually contains some impurity which renders it unsuitable for use. (The trouble may be caused by ammonia. Winkler (*Z. angew. Chem.*, 1916, xxix., i., 18) describes a method of removing this. According to Delépine, (*Jahrb. Chem.*, 1892, p. 196, ammonia raises the density of alcohol).

*Barium oxide* appears to act more rapidly than lime, presumably, again, because it forms alcoholate more readily, at least with some alcohols. We have not found that it dries the alcohols more thoroughly than lime, which is not surprising, since any further reduction in the amount of water below what can eventually be reached lime, probably could not be detected.

*Aluminum amalgam*, recommended by Wislicenus and Kaufmann (Wislicenus, *Ber.*, 1895, xxviii., 1323; Kaufmann, *J. prakt. Chem.*, 1896, [2] liv., 54), we have found to be very effective. It dries butyl alcohol, with which it forms alcoholate readily, much more rapidly than *iso*-propyl alcohol, with which the alcoholate formation is slow. In view of the fact that aluminum hydroxide dissociates partially at 200°, it would appear that the dissociation pressure of water might be sufficient at 117° to prevent thorough drying of the alcohol. There is, perhaps, not conclusive evidence that aluminum oxide rather than hydroxide is not formed, or possibly a partially hydrated oxide. Some of our best tests were made with this drying agent, and although we did not discover that lime or baryta did not eventually produce the same result, the aluminum hydroxide it nevertheless the most satisfactory reagent we found, on account of rapidity of its action.

*Densities.*—The densities have been determined with a pycnometer of the Sprengel type, with arms bent up and thermometer fused in, with a capacity of 8·2760 cc. at 25°. The thermostat is controlled to ±0 02° or better. To protect the liquid in the pycnometer from a fine, hardly visible spray thrown up by the vigorous stirring of the thermostat, small glass tubes, closed at the outer end, were fitted loosely over the arms. Without these it appeared that the density altered slightly when the pycnometer remained long in the thermostat. The density determinations are accurate to ±0·00002.

*Refractivities.*—The refractivities were determined with a Zeiss-Pulfrich refractometer. Accuracy to the fourth decimal in absolute value of the refractive index is barely obtainable with our instrument, although occasionally a 5 in the fifth decimal is thought justifiable. Constant temperature was secured by a slow current of water run through a copper coil in the thermostat.

As regards the relative value of the various physical properties as a criterion for the purity or identity of such substances, it is to be noted that we have had no difficulty in preparing specimens agreeing in boiling point to 0·01°. The agreement in refractivity to the fourth decimal has also frequently been satisfactory. Nevertheless, the determination of the density to the fifth decimal has in some cases shown such specimens not to be identical. If these are assumed to be, respectively, the degrees of accuracy easily attainable in the determination of these constants, it is evident that the densities are the best test of the purity of the substances.

*Preparation of alcohols.*—Ethyl, *n*-propyl, *n*-butyl, and *iso*-butyl alcohols were the best commercial products obtainable.

The secondary alcohols here described, as well as others not yet fractionated, were prepared by catalytic reduction of ketones under pressure, with nickel oxide as catalyst. The method is, in principle, that of Ipatiew (*C.A.*, 1907, i., 2878, and other articles in the *J. Russ. Phys. Chem. Soc.*), although the apparatus was designed by Bergius

(somewhat like that described by Bergius, *Dissertation*, Halle, 1913).

The bomb is a steel tube, 60 cm. long, and 30 mm. inner diameter, with 1 cm. walls, rotated in a horizontal position in an electric furnace. The capacity is 260 cc., and it is usually half-filled with ketone. The reduction goes on rapidly at any pressure above about 45 kg., at temperatures of 150-200°, but in order to accelerate the reaction, as well as from the necessity of introducing the requisite quantity of hydrogen, an intial pressure of 1363 kg. is usually used. This quantity of hydrogen will react completely in less than 10 minutes.

This method has several advantages over that of Sabatier and Senderens and their collaborators, once the apparatus is installed. The catalyst may be prepared with much less care, nickel nitrate being heated to redness; the oxide need not be reduced to metallic nickel; commercial electrolytic hydrogen is pure enough, and oxygen need not be excluded with particular care; by taking care that there is an excess of hydrogen (usually about 230 kg.) during the final heating, the reaction, which is reversible, can be driven practically to completion and 130 cc. of almost pure alcohol can be prepared per day.

*Experimental part.*

All of the boiling points recorded have been reudced to 760 mm. to facilitate comparison. Since the values recorded in the literature for $dT/dp$ are not in agreement, even for ethyl alcohol, we have used values deduced from the boiling points of our own specimens on different days. The disagreement in the values found for $dT/dp$ is doubtless due to the fact that this property is very susceptible to the influence of impurities if their boiling point differs greatly from that of the alcohol.

The boiling points in the determinations with the thermoelement were in some cases constant to 1 $\mu$v. (0·002°), or less. Where they were not constant, the temperature given is the maximum and the magnitude of the fluctuation is indicated. The values obtained by the authors at the Bureau of Standards are also given. The differences between these values and those eventually obtained are doubtless due to the moisture of the specimens. These values are, however, near enough to those obtained with the thermoelement to show that there is no error of great magnitude in either set of values.

Where distillation with the thermoelement is mentioned, the data refer to the distillation of small specimens from the boiling-point apparatus.

Complete data are given for the final distillation of many of the specimens. In particular, they are given where the constant boiling portion of the distillate was divided into several fractions. The temperature ranges for the fractions are based on the thermometer readings, but the actual temperatures are all corrected in accordance with the best value obtained for the boiling points.

*Ethyl alcohol.*—Boiling point: (1) thermoelement: aluminum amalgam, 78·317° (77·979° at 750·35 mm.); (2) thermometers: 78·31°, 78·32°, 78·33°; mean,: 78·32°; (3) obtained by the authors at the Bureau of Standards, 78·42°. The best specimens distilled entirely at constant temperature, except for less than a grm. at the beginning.

*n-Propyl alcohol.*—Boiling point: (1) thermoelement: aluminum amalgam, 97·19° (0·01°); (2) thermometers: 97·19°, 97·19°, 97·17°; (3) obtained by the authors at the Bureau of Standards, 97·12°.

In view of the particularly numerous and discordant values for the physical properties of propyl alcohol recorded in the literature, the following data for the distillation of our best specimen are given.

A. Weight before distillation, 216 g. I. 97·04—97·17°; 5 g. II. 97·17-97·19°; 27 g. III. 97·19°; 114 g.

The temperature remained constant until the distillation stopped, but the amount of alcohol left in the still was much larger than usual. Data for our other specimen are given in Table I. below.

*Iso-propyl alcohol.*—Boiling point: (1) thermoelement: boiled 4 hours with lime and distilled, 82·239-82·263°; boiled 6 hours with lime and distilled; 82·257-82·267°; boiled 4 hours with aluminum amalgam, 82·259° (0·004°); (2) thermometers, 82·27°, 82·28°, 82·29°; mean: 82·28°; (3) obtained by the authors at the Bureau of Standards, 82·25°.

This alcohol was distilled in glass columns for fear of re-oxidation by contact with the brass, but this was later found to be a needless precaution. The data for the best specimen (A) are as follows: wt., 210 g. I., 82·12-81·25°; 8 g. II., 82·25-82·26°; 14 g III., 82·26°; 147 g. IV., 82·26°; 30g.

The data for physical properties of other specimens are given below.

*n-Butyl alcohol.*—Gentle boiling with the drying agent does not dry the alcohols boiling above 100°, since the water distils out of the liquid and remains in the condensate in the upper part of the apparatus. It is necessary occasionally to boil the alcohol up vigorously and wash the apparatus down.

Boiling point: (1) thermoelement: boiled with barium oxide, 117·706° (0·003°); same 117·707°, maximum, not constant; metallic calcium, 117·712° (fluctuations, 0·01°) (this was not a very reliable determination, and does not indicate inferiority of the calcium as a drying agent). Aluminum amalgam, 117·705° (0·003°); same, 117·707° constant; (2) obtained by the authors at the Bureau of Standards, 117·686°.

For the alcohols above 110°, the values obtained with the thermometers during the distillation are in such disagreement as to be of no value. In this case they disagreed by over 0·1°.

Data for distillation of two specimens from different sources follow: (A) I., 117·69-117·70°, 19g.; II., 117·70-117·71°, 16 g.; III., 117·71°; 303 g. (B) wt., 610 g. I., 117·54-117·64°, 9 g.; II., 117·64-117·67°, 36 g.; III., 117·67-117·70°, 45 g.; IV., 117·70-117·71°, 28 g.; V., 117·71°, 251 g.; VI., 117·71°, 103 g.; VII., 117·71°, 65 g. V., VI., VII., total, 419 g.

The low boiling fractions in B are larger than they should have been owing to poor control of the rate, which reached 100 drops a minute at times. To secure small low boiling fractions it is advantageous to conduct that part of the distillation very slowly. The constant boiling portion in B was again divided.

(To be continued).

## PRESENTATION TO DR. FREDERICK BELDING POWER

(Late Director, Wellcome Chemical Research Laboratories London).

The presentation of a medal, conferred by Mr. Henry S. Wellcome, took place in the Assembly Hall of Cosmos Club, Washington, U.S.A., on May 9, 1921.

Dr. DAVID FAIRCHILD opened the meeting by reading letters from the following gentlemen, expressing regret for their inability to attend the presentation: Dr. Thomas B. Osborne, of New Haven, Conn., Prof. Marston T. Bogert, of Columbia University, New York City, Prof. Chas Baskerville, of the College of the City of New York, Prof. W. A. Noyes, of the University of Illinois, Prof. Rodney H. True, of the University of Pennsylvania. After reading the letters he stated that the meeting was open.

Dr. CHARLES D. WALCOTT, Secretary of the Smithsonian Institution, and President of the National Academy of Sciences, then read the following presentation address.

"Ladies and Gentlemen—We have gathered here this afternoon to do honour to Dr. Frederick Belding Power, who, for 50 years, has spent his thinking hours among the complicated molecules of organic compounds; who, because he possesses that peculiar faculty of exhausting each subject which he takes up, has had the greatest influence both in America and Great Britain in raising the standard of our pharmacopœias; who has gained distinction by his most difficult and life-consuming researches into the chemical composition of plant compounds.

As a lasting tribute to these 50 years of research and in commemoration of those which he spent as Director of the Wellcome Chemical Research Laboratories of London, I have been asked by Mr. Henry S. Wellcome, their founder, to present him with this gold medal, which bears the following inscription: "To Frederick B. Power, PhD., LL.D., in recognition of his distinguished services to science during 18½ years as Director of the Wellcome Chemical Research Laboratories, London. Presented by the founder, Henry S. Wellcome, 1914."

Dr. Power graduated from the Philadelphia College of Pharmacy in 1874, in the same class with his life-long friend, Mr. Wellcome, who urged him to pursue his studies in Germany. He spent the years from 1876 to 1880 in Strassburg, becoming the assistant to Flueckiger, one of the greatest pharmacologists of Europe. Returning to America, he spent nine years in the organising and building up of the Department and School of Pharmacy in the University of Wisconsin, four years in researches on essential oils in a newly-organised chemical works near New York, and in 1896 Mr. Wellcome appointed him Director of his chemical research laboratories in London. For 18½ years he devoted his time exclusively to chemical research, and the direction of a staff of research workers under him. 170 important scientific memoirs were published from the laboratories during this period. These covered a wide field of investigation, for which material was obtained from all parts of the world. Among these a very notable and complete study was made of the East Indian chaulmoogra oil, which resulted in the discovery of some physiologically active acids of an entirely new type. These form the basis of the new treatment of leprosy which gives promise of effecting a complete cure of one of the most terrible diseases of mankind.

During these years in London, Doctor Power had the opportunity of meeting and forming the close friendship of the foremost scientific men of Great Britain. The recogniton of his work by the leading chemists and other scientists of Europe would be perhaps exemplified in the high tribute paid to him by the late Lord Moulton, one of the most learned and versatile men in Europe, who was entrusted by Kitchener with the task of producing the high explosives for the war. Shortly before his death, he chided Mr. Wellcome for permitting Dr. Power (who for family reasons had returned to America) to leave Great Britain, for, as he remarked, "there was no one in Europe who could fill his place."

In 1908, the University of Wisconsin, commemorating the 25th anniversary of the formation of its Department of Pharmacy, conferred upon Dr. Power, its founder, the degree of LL.D., and in 1913 the Chemical, Linnean and Pharmaceutical Societies of London awarded him the Hanbury Gold Medal, a distinction only once previously bestowed upon an American. This was followed by the presentation of an illuminated address and an album containing the signatures of contributors from many parts of the world.

Dr. Power, in recognition of your distinguished services to science and in commemoration of the years which you spent as Director of a laboratory devoted to chemical research, I have the honour to present to you this gold medal of appreciation from your life-long friend, Mr. Henry S. Wellcome, who, although with us this afternoon, is unfortunately prevented by a severe throat affection from addressing us himself. In presenting it he wishes to explain that war conditions have prevented its earlier execution and presentation."

Dr. POWER acknowledged the medal as follows: "Dr. Walcott, I feel it to be a great honour to receive at your hands the beautiful medal which my friend, Mr. Wellcome, has so kindly and generously bestowed upon me, and I deeply appreciate the sentiments which you have so eloquently expressed concerning my work. I can assure you, Dr. Walcott and Mr. Wellcome, that this memento will always be regarded by me as one of my most precious possessions. It is difficult and well-nigh impossible on an occasion such as this to express adequately in spoken words the thoughts that are uppermost in my mind, for there are many happy recollections when a friendship formed in boyhood has continued uninterruptedly during a period of nearly half a century. I cannot but be reminded that it is just 25 years ago this month when I left America for London to undertake the organisation of the Chemical Research Laboratories which Mr. Wellcome desired to establish, and that the first public announcement of his purpose was made on the evening of July 21, 1896, in a beautiful salon of the great metropolis, where, by the invitation of Mr. Wellcome, a number of the most distinguished scientific men of England were asesmbled, whom it was my privilege to meet. One of the guests on that occasion was the late lamented Lord Moulton, whose brilliant legal

career and service to science, especially during the strenuous years of the war, have won for him an enduring fame. The work that was so auspiciously inaugurated on that July evening it was my privilege to conduct for a period of 18½ years, and, although years of hard and earnest toil, they were replete with happy associations, and I trust, not without some benefit to the science that it was my endeavour to serve.

There is one dominating thought that I should like particularly to convey to my friend Mr. Wellcome, and that is embodied in an expression of gratitude. I am grateful for the encouragement and inspiration received from him on our journey through life, for we have travelled long and far together, but above and beyond all, I am grateful for having possessed through so many years so kind, generous, and true a friend For this latest expression of your kindness, Mr. Wellcome, I beg you to accept my warmest thanks, and I desire also to extend my hearty thanks to Dr. Walcott for having so happily conveyed to me your beautiful gift."

Dr. WALCOTT then adjourned the formal meeting after inviting all those present to meet Dr. Power, and to add a word of personal appreciation to those given formally. A social hour followed, with light refreshments.

## PROCEEDINGS OF SOCIETIES.

### SOCIETY OF GLASS TECHNOLOGY.

THE May Meeting of the Society of Glass Technology was held in the Applied Science Department, the University, St. George's Square, Sheffield, on Wednesday, May 18, 1921, at 2.30 p.m., the President, Dr. MORRIS TRAVERS, F.R.S., in the Chair.

The first paper was entitled "*The Shrinkage, Porosity, and Density of British Fireclays after Firing at* 1500° *C.*" By EDITH N. FIRTH, B.Sc. and W. E. S. TURNER, D.Sc. The paper was illustrated by lantern slides and by specimens.

Prof. Turner, who gave the paper, said :"The paper and the data which are to be presented represent a continuation of the work which has been done, and details of which were supplied a year ago here at Sheffield, on certain physical properties of British clays taken from different sources throughout England, and one or two sources in Scotland. The first paper gave an account of certain general characteristics, and the amount of shrinkage which was observed when samples of these clays were heated at various temperatures up to 1400° C. In addition to the shrinkage, the porosity of the different samples was determined, and two other properties, perhaps of less importance, namely, the density, both actually of the clay itself, and the apparent density of the fired pieces. Another point in connection with the tests mentioned at the time was that the firing was not carried out by heating the clay slabs up in company with a seger cone and then taking out the slabs as soon as the certain cone had begun to squat, but the slabs were heated up in an electrically-fired furnace until the shrinkage remained constant. It was the desire of the workers, and certainly necessary for information's sake, especially in the somewhat hotter furnaces used in the glass industry, that the measuring should be carried to a still higher stage, in fact, at as high a temperature as possible. Attaining a higher temperature, especially beyond 1400° C., is by no means easy, but at any rate, measurements have been carried out at 1500° C. We hope that a still further stage may be reached at some time. Results presented deal with the same set of clays as previously, 27 of them in number, and they have had their shrinkages and their porosities, as well as the actual density and the apparent density determined between 1400° and 1500° C. Some further change occurs with all the samples. Consider first of all the shrinkage. In eight cases there is not a further contraction, but an actual expansion; the shrinkage is negative In the case of the porosity there are two only which show a distinct increase in porosity between 1400° and 1500° C., all the remainder showing either small or in some cases quite a large diminution of porosity.

In regard to the actual extent of the shrinkage where further shrinkage was found, it was considerable in the case of the Ayrshire bauxitic clay, Wortley clay, one of the Yorkshire clays, and also one of the Stourbridge clays In regard to the porosity, the two clays which give an increased porosity are both of them Yorkshire clays.

Now increased porosity is a change which is not to be desired because it will usually be a sign of the phenomenon of blistering, which takes place when clays are heated above a certain temperature; that is to say, are "over-fired." What takes place precisely at this point we have no very precise information, other than this, that the material gets spongy, not only the surface, but the interior mass begins to swell, and loses its value as a refractory material. There are some seven clays which show blistering, and therefore are not usable outside the range between 1400° and 1500° C. Those clays are Kilmarnock, Wortley, a German clay (Grossalmerode), two Halifax clays, and two Stourbridge clays, the worst being Halifax clays. In five out of the seven clays the blistering is only at the surface. There is a general swelling developed in two of them. These are the two Halifax clays. That means that they are not capable of being used beyond the 1400° limit.

It has been shown in the first place that 25 out of 27 of the samples of British clays, excluding for the moment Grossalmerode, are capable of being used between 1400° and 1500°. This does not mean to say that they should all be used. Of these 25, six undergo expansion between 1400° and 1500° C.; in other words, their behaviour becomes somewhat irregular, perhaps somewhat anomalous, and on that ground one would perhaps avoid using them.

Besides the results stated, the actual structure of the burnt pieces needs to be examined. Some of these samples have been sent on to Mr. G. V. Wilson, who has previously done valuable work for the industry, and we hope he will examine them. Our President, Dr. Travers, was also making some valuable suggestions during the lunch hour about the possibility of X-ray examination, and I hope it may be possible for this examination, as he suggests, to be carried out."

The second paper was entitled *"The Effect of he Rays from Radium, X-rays, and Ultra-violet Rays on Glass."* By J. R. Clarke, M.Sc., F.Inst.P.

The results obtained by previous workers are summarised, and then experiments, which were carried out in order to ascertain the effect of particular oxides, and to see whether the concentration of the oxide had any influence on the colour, are described. Seven lime-soda glasses, three of which contained selenium, and three cobalt, were exposed to the action of the $\alpha+\beta+\gamma$-rays, $\beta+\gamma$-rays, $\gamma$-rays, X-rays, and ultraviolet rays. The first six were coloured brown by the $\beta$-rays, and the depth of coloration corresponding to the range of the $\beta$-particles in the glasses, and the intensity of the coloration being greatest on the surface and decreasing towards the interior; it increased with increased selenium and cobalt content. As the radiation was prolonged, the intensity increased to a maximum, which depended on the percentage of colouring agent, and then remained constant; the intensity in the interior tended towards the same maximum as that on the surface. The seventh, pure lime-soda glass, was only affected by the $\alpha$-rays, being faintly coloured on the surface only. None of the glasses were coloured by $\gamma$-rays, X-rays, or ultraviolet rays with the exposures given.

All the glasses fluoresced when kept in radium emanation, but a "fatigue" effect was observed at about the same time as the maximum intensity of coloration was reached. It is thought that the $\alpha$-rays are the chief agents in producing fluorescence, though the $\beta$-rays are also effective. None of the glasses fluoresced under the action of X-rays, but the pure lime-soda glass and the selenium glass fluoresced slightly when exposed to ultraviolet rays. All the glasses exposed to radium emanation exhibited thermoluminescence with disappearance of colour at temperatures of 100°, 160°, and 235°.

The colouring of the glasses is concluded to be due to the formation of colloidal particles in the glasses. It is suggested that the presence of such particles may be explained by the action of the $\alpha$- or $\beta$-rays on dissociated ions already present in the glasses. The fluorescence is held to be due to mechanical bombardment of the glass molecules by the rays.

## SOCIETY OF PUBLIC ANALYSTS.

*Ordinary Meeting June* 1, 1921.

Mr. Alfred Smetham, President, in the Chair.

A Certificate was read for the second time in favour of Mr. W. N. Stokes, B.Sc., A.I.C.

The following were elected Members of the Society: Messrs. Thomas Henry Pope, B.Sc., F.I.C., William Ellard Woolcott.

The following papers were read:

*"The Composition of Egg Powder."* By F. F. Beach, T. E. Needs, and Edward Russell, B.Sc., F.I.C.

The authors record the results of the examination of the so-called egg powders, comparing them with ordinary baking powders. A table of compositions is appended and it is suggested that a standard based on certain specified figures might be laid down for a minimum percentage of actual egg in such preparations.

*"The Colorimetric Method of Determining Hydrogen-Ion Concentration: Some Uses in the Analytical Laboratory."* By Norman Evers, B.Sc., F.I.C.

The colorimetric method of determining hydrogen-ion concentration by means of indicators is described. Examples are given of its usefulness in replacing titration methods in the determination of the "acidity" or "alkalinity" of various products, and of the purity of certain fine chemicals.

*"The Estimation of Woody Fibre in Cattle Foods."* By F. Robertson Dodd, F.I.C.

The author, referring to the discrepancies between the results of different analysts working on the same sample by varying processes, suggests a modification of the method which would tend to obviate this.

*"The Spectrometric Examination of Certain Fixed Oils as a Means of Identification."* By H. C. T. Gardner.

The author's observations go to show that mere spectroscopic examination of a fixed oil is not of itself sufficient, but that evidence of identification can be obtained, in the case of certain oils, by measuring the positions of the terminations of visibility, together with the extent of visibility of the absorption spectra of various oils. Generally dissimilar oils exhibit dissimilar limits of visibility of their spectra.

## NOTES.

Royal Institution.—A General Meeting of the Members was held on June 6, Sir James Crichton-Browne, Treasurer and Vice-President in the Chair. Miss G. Caton-Thompson, Sir John Collie, Mr. N. G. Hallett, Dr. H. R. Le Sueur, Mrs. Sidney Turner, Mr. J. Whitehead, and Dr. Leonard Williams were elected Members. The special thanks of the Members were returned to Sir Humphry Davy Rolleston for his present of a safety lamp which was in the possession of Dr. John Davy, brother of Sir Humphry Davy, and to Sir David L. Salomons for his present of a privately-printed "Life and Study of the Works of Breguet, the famous Watchmaker"; Arago's watch and two others of special interest, the first working aneroid made by Vidi in 1857, and a series of models illustrating the development of the chick.

Conjoint Board of Scientific Societies.—The Fourth Report of the Conjoint Board shows that the Board has received evidence that scientific investigation is being seriously hampered by the heavy cost involved in the publication of results. An exceptional number of papers are being communicated to the scientific societies, including many held up during the war, while the resources of the societies, which have not increased, are insufficient at present prices to publish even the normal pre-war number. The country is thus in

danger of being seriously handicapped at a time when the rehabilitation of industry is in most serious need of scientific assistance. Much of the Report is occupied with a short abstract of the Third Report of the Committee on the "Water Power of the Empire." It is shown that too little is being done to ascertain the total resources, or to secure uniformity in investigation and record. It is urged that steps should be taken to convene an Imperial Water Power Conference in London, at which the various Dominions and Dependencies of the Empire should be represented. The outcome of such a conference might well be the creation of an Imperial Water Power Board with extensive powers to carry out a comprehensive policy for stimulating, co-ordinating, and where necessary assisting development throughout the Empire. The Board has also dealt with questions relating to the formation of National Reserch Committees, in connection with the International Research Council formed in 1919, with the collection of scientific data in the former German colonies, and with instruction in technical optics. The research on glues and other adhesives initiated by the Board as a war measure, at the instance of the Air Ministry, has now been taken over by the Department of Scientific and Industrial Research.

TENDERS INVITED FOR CALCIUM CARBIDE.—Tenders are invited up to noon on July 15 next by the Egyptian Postal Administration at Alexandria for the supply of 15,000 kg. of calcium carbide for acetylene gas light plants. Quotations should comprise free storage at the sole risk of the contractor, and free delivery (by periodical partial supplies during the year) at 62 railway or river stations specified. Representation by a resident local agent is necessary, but United Kingdom firms not represented may care to avail themselves of the services of firms with an Egyptian branch whose names can be obtained at the Department of Overseas Trade, 35, Old Queen Street, London, S.W.1. A copy of the above-mentioned specification is also available for inspection by United Kingdom manufacturers on application to the Enquiry Room of the Department.

ARTIFICIAL RESIN.—The artificial resin of C. C. Bohler is prepared by heating anhydroformaldehydaniline singly or mixed with small quantities of acids or alkalies, organic or mineral, at 100° to 200° C., and causing a reaction of vulcanising reagents, during formation of the resinous substance, especially sulphur chloride, with the mixture of reaction or the final product. Example: Heat 100 parts of anhydroformaldehydaniline, ½ part concentrated $HNO_3$ and 1 part sulphur chloride first to expel water, and then until the moment of obtaining the degree of hardness and fusion point required, at 100° to 200° C. For vulcanisation sulphur and selenium can be employed or their soluble compounds.—*Matières Grasses*, Feb. 15, 1921.

CATALYTIC HYDROGENATIONS ON COPPER.—One of the experimenters, Messrs P. Sabatier and Bennosuke Kubota, demonstrated that copper obtained by slow reduction at 200° C., of hydrated copper oxide was a hydrogenating catalyser ("La Catalyse," 2nd edition). Continuing this study, the authors demonstrate that the aldehydes and aromatic cetones lead to carbides. With acetophenone one obtains ethylbenzene at 350° C. Hydrogenation of benzoquinone gives hydroquinone; that of phtalic anhydride phtalides with toluene, carbon monoxide and water.—*Comptes Rendus*, March 21, 1921.

RECORDING CHEMICAL REACTIONS ACCOMPANIED BY PRESSURE, BY PHOTOGRAPHY.—Temperature of the reaction and corresponding pressure can be simultaneously recorded (P. Jolibois). The pressure is measured with an electric current intensity which is recorded by photography of the spot of a galvanometer. For this purpose a well-gauged platinum wire is placed in the manometer, inserted in the circuit of a Daniell element. When the mercury rises in the manometer, the length of the wire is diminished, and consequently the resistance of the circuit. Intensity increases with pressure. A clock which periodically breaks the luminous pencil enables one to mark the time on the clichés.—*Comptes Rendus*, March 29, 1921.

## NOTES AND QUERIES.

A CORRESPONDENT asks for information as to the process employed for producing a frosted or silky surface upon glass by means, other than sand-blasting.

## NEW COMPANIES.

The under-mentioned particulars of New Companies recently registered are taken from the Daily Register compiled by JORDAN & SONS, LIMITED, Company Registration Agents, Chancery Lane, W.C.2.

SIDUCOS, LIMITED.—(174863)—Registered 25th May, 1921. To carry on the business of Chemists and Druggists. Nominal Capital. £10,000 in 10,000 Shares of £1 each. Directors: To be appointhd by Subscribers. Remuneration of Directors: £50 each. Chairman: £100. Subscribers: H. H. Walton, 275, Croxted Road West, Dulwich, S.E.; M. Hackforth-Jones, Arkley House, Barnet, Herts.

T. W. RANSON, LIMITED.—(174867)—Registered 25th May, 1921. 7, Brazennose Street, Manchester. To carry on the business of Manufacturers and Dealers of all kinds of Chemical including Manures, Bones, Slag and Substances allied thereto. Nominal Capital £5,000 in 5,000 Shares of £1 each. Directors: T. W. Ranson, Westwood, Church Road, Urmston, P. A. Ranson, Westwood, Church Road, Urmston. Qualification of Directors: £1. Remuneration of Directors: To be voted by Company.

W. J. LEWIS, LIMITED—(174838)—Registered 23rd May, 1921. 3, Hinckley Road, Leicester. To acquire and carry on the business of Pharmacists and Dispensing Chemists Nominal Capital: £5,000 in 5,000 shares of £1 each. Directors: E. A. A. Fry, 65, Hoard Road, Leicester; S. J. Farr, 35, Herschell Street, Leicester. Qualification of Directors. 100 Shares. Remuneration of Directors: To be voted by Company.

## New Patents.

THIS List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W.C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

13981—Chemische Fabrik vorm Sandos.—Process for manufacture of a new preparation of hexame-thylenetetramine. May 18th.

13812—Nitrogen Corporation.—Preparation of hydrogen and ammonia. May 17th.

14035—Soc. Anon. de Produits Chimiques Etablissements Maletra.—Continuous production of sulphates. May 19th

14049—Soc. Anon. de Produits Chimiques Etablissements Maletra.—Process for production of acetaldehyde from acetylene. May 19th.

*Specification published this Week.*

163162—Ellis, G. B.—Purification of ammonium salts.

*Abstract Published this Week*

*Lithopone.*—Mr. R. Le Baker of St. Louis, U.S.A., has been granted a Patent No. 161280 in this country for an improved process of obtaining lithopone by the mutual precipitation of zinc sulphate and barium sulphide, the zinc sulphate solution is first freed from iron by a preliminary heat and oxidation treatment in the presence of an alkaline-earth peroxide such as barium or calcium peroxide and lead or zinc monoxide. The zinc-sulphate solution in the tank which is fitted with an agitator and is supplied with steam from a pipe, and compressed air from the tank, is treated with the powdered peroxide and zinc or lead monoxide in the proportion of about 1 per cent of the zinc sulphate in solution. The liquor is then passed through the filter-press to the tank where it is again treated with steam and air. After filtration which does not move the finely divided hydrated zinc oxide, the liquor is mixed with an equivalent quantity of barium sulphide solution in tank. The resulting precipitate is filtered off, washed, dried, calcined, quenched in cold water and ground wet. After another washing the pigment is filtered and dried.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

## MEETINGS FOR THE WEEK.

*Wednesday, June 15.*

Royal Microscopical, 5.

*Thursday, June 16.*

Royal Society. "Velocity of Sound in Gases at high Temperatures, and the Ratio of the specific Heats," by H. B. Dixon, Colin Campbell and A. Parker. "The Ratio of the specific Heats of Air and of Carbon Dioxide," by J. R. Partington. "'Light Body' Hydrophones and the directional Properties of Microphones," by A. B. Wood and F. B. Young. "Acoustic Disturbances produced by small bodies in Plane Waves transmitted through Water, with special reference to the single Plate Direction Finder," by A. B. Wood and F. B. Young. "Some Problems connected with Evaporation from large Expanses of Water," by M. A. Giblett. "The Photographic Efficiency of Heterogeneous Light," by F. C. Toy.

Chemical Society, 8.

*Friday, June 17.*

Royal Institution, 9. "Chemical Combination and the Structure of the Molecule," by Sir J. J. Thomson.



## NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemical Apparatus, &c., for review or notice to be addressed to the EDITOR.

**SUBSCRIPTIONS,** £1 12s. per annum, payable in advance, should be addressed to the MANAGER.

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THE CHEMICAL NEWS,
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## ADVERTISEMENTS.

**All communications for this Department should be addressed to—**

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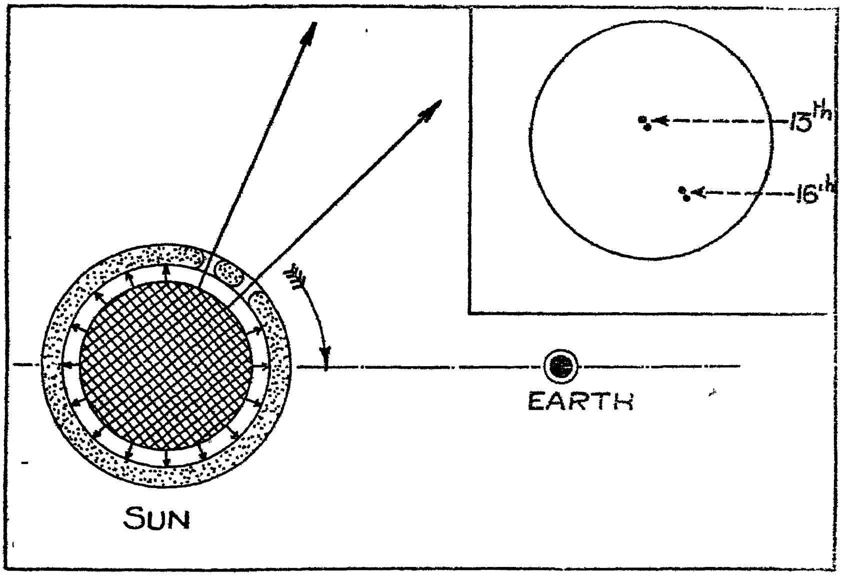
THE CHEMICAL NEWS.
VOL. CXXII, No. 3192.

# ATOMIC ENERGY AND SOLAR RADIATION: SUN-SPOTS AND AURORA.

By F. H. LORING.

THE origin of the aurora in the polar regions where the magnetic pole plays an important part in giving rise to various electrical effects, as seen in the vacuum tube, has led to certain investigations of this phenomenon. Some of these experiments will be briefly noted below; but first, an early account of the aurora itself, as given by Humboldt, is of interest, and it will serve to remind the reader of the complexity and beauty of the phenomenon.

"An Aurora Borealis [*Northern Light*, or *Polar Light*; there is also an *Aurora Australis*] is always preceded by the formation in the horizon of a sort of nebular veil, which slowly ascends to a height of 4°, 6°, 8°, and even 10°. It is towards the magnetic meridian of the place that the sky, at first pure, commences to get brownish. Through this obscure segment, the colour of which passes from brown to violet, the stars are seen as through a thick fog. A wider arc, but one of brilliant light, at first white, then yellow, bounds the dark segment. Sometimes the luminous arc appears agitated for entire hours by a sort of effervescence and by a continual change of form before the rising of the rays and columns of light which ascend as far as to the zenith. The more intense the emission of the polar light the more vivid are its colours, which from violet and bluish-white pass through all the intermediate shades of green and purple-red. Sometimes the columns of light appear to come out of the brilliant arc mingled with blackish rays similar to a thick smoke. Sometimes they rise simultaneously in different points of the horizon; they unite themselves into a sea of flames, the magnificence of which no painting could express, and at each instant rapid undulations cause their form and brilliancy to vary. Motion appears to increase the visibility of the phenomenon. Around the point in the heaven which corresponds to the direction of the dipping needle, the rays appear to assemble together and to form a boreal corona. It is rare that the appearance is so complete and is prolonged to the formation of the corona, but when the latter appears it always announces the end of the phenomenon. The rays then become more rare, shorter, and less vividly coloured. Shortly, nothing further is seen on the celestial vault than wide, motionless, nebulous spots, pale, or of an ashy colour; they have already disappeared when the traces of the dark segment, whence the appearance originated, are still remaining on the horizon."




De la Rive was probably the first one to suggest that the aurora was an electrical effect as exhibited in Geissler's tubes, especially under the modifying influence of a magnet.

Sabine showed that there is a period of maximum frequency of magnetic storms and aurora which coincide with the maximum appearance of sun-spots.

Birkeland devised experiments by which he demonstrated that the magnetic storms could be imitated by placing a spherical body with magnetic poles—termed a *terrella*—inside a vacuum tube, the cathode representing the sun. For example, during an equatorial storm when the horizontal magnetic component is decreased, the conditions can be demonstrated by means of the terrella, which corresponds to the earth. In this case the cathode rays encircle its magnetic equator.

Störmer, in co-operation with Birkeland, worked out the trajectories of the electrified particles on entering the earth's field, the results of which support Birkeland's theory that the phenomenon arises from charged particles ejected from the sun.

Villard, in 1906, showed that cathode rays, as

influenced by a magnetic field, give rise to effects identifiable with those of the aurora. D. Owen gives in his book ("Recent Physical Research," 1913, chap. vi) an account of some of the above experiments. See also Rutherford, "Radioactive Substances and their Radiations," 1913, p. 654; the following references to literature being given: Birkeland, *Arch. d. Sci. Geneva*, 1896; The Norwegian Aurora Polaris Expedition, 1902-3; Stormer, *Arch. d. Sci. Geneva*, 1907, 24; Vegard, *Phil. Mag.*, 1912, xxiii., 211; Darwin, *Nature*, 1903, lxviii., 496.

V. M. Slipher (*Astrophys. Journ.*, 1919, xlix., 266) gives evidence of the constancy of the phenomenon indicating that normally the sun emits (according to the views here presented) a sufficient number of electrified particles to cause weak effects—in fact, in polar regions the aurora is a regular occurrence. Slipher states that during a period of 3½ years, 100 spectrograms were taken at the Lowell Observatory, of the night sky, and each one gave the chief auroral line. The wave-length of this line was found to be 5578·05. It had been thought that this line was due to the nitrogen pair λλ 5560-5565 (see Stark, *Ann. d. Physik*, 1918, liv., 598), but this supposition seems no longer tenable.

Passing now to sun-spot phenomena, the following from the *Encyclopædia Britannica* will serve to introduce the subject: "Each spot shows, as a rule, one or more spots or groups of spots. Each spot shows with more or less completeness a ring-shaped penumbra enclosing a darker umbra; the umbra, which looks black beside the photosphere is actually about as brilliant as lime light." This appearance can be illustrated by dropping a drop of blue-black ink on a piece of paper; and, after blotting, dropping a small drop of Indian ink on top of the spot so as to leave a blue-black margin. This margin, of course, represents the penumbra.

A. L. Cortie (*Astrophys. Journ.*, 1907, xxvi., 123), referring to the band spectra, due to radiation from sun-spots, and their identification as flutings, remarks on the existence of chemical compounds. For bands at the extreme red have been identified by Hale and Adams (see W. S. Adams, *Astrophys. Journ.*, 1909, xxx., 86) as produced by titanium oxide, and later, Fowler has ascribed the bands in the green part of the spectrum to magnesium hydride. The observed change in the spectrum of Mira Ceti—as the brightness and temperature of this star had increased, its band spectrum had gradually changed more to a line one—affords evidence that the band spectra of the sun-spots indicate a temperature of the vapour therein which is lower than that of the photosphere.

Referring to the upper figure of the accompanying diagram, this represents the spots as they appeared during the interval, May 13-16, 1921, when seen through an opera-glass, the sun being low, and slightly dimmed by haze. The change in position seems to agree with the sun's rotation (25 days, 9 hours, 7 minutes), but no attempt is made to produce an accurate drawing. Accompanying the recent auroral display there was a magnetic storm of unusual violence, which was recorded in the Press at the time.

Referring to the other diagram (not drawn to any particular scale, and not intended to conform to any detailed features of the sun's structure, some of which are superficially known) it will be seen that as the spots revolve, the ejected matter (see previous paper in this Journal, vol cxxii., p. 219) represented by the long arrows, will pass within range of the earth and come under the influence of its magnetic field, so that, assuming the ejected matter to be electrically charged particles, when they strike into the earth's atmosphere, they will give rise to the aurora.

The blackness of the spots, perhaps, has a partial analogy in the Faraday and Crookes dark spaces, as seen in vacuum tubes, especially as according to the views here advanced the whole phenomenon is a bombarding process involving positive-rays, or atomic nuclei and probably negative electrons. The radial arrows shown in the figure are intended to illustrate the bombardment or general course of these rays.

There seems to be some evidence that the sunspots are due to a species of eruption which has its origin in the nucleus of the sun. A gas composed of the above-mentioned particles might accumulate in large quantities in the central part or core of the sun, and work out gradually to the surface The sunspot period of maximum activity is 11 years, which corresponds to about 158 revolutions of this body on its axis.

A thinning of the envelope may take place at times or in areas, and considerable quantities of the particles of disintegration may pass completely away from the sun. This would perhaps account for magnetic storms when the spots are not in particular evidence, and certainly it would seem to account for the auroral line always being present in the night sky.

The spots show evidences of being centres of powerful cyclonic disturbances, but the entire surface of the sun is in violent agitation, and the prominence flames have been known to extend outwards 150,000 miles. The whole phenomenon is on such a gigantic scale one can hardly realise its magnitude. The spots themselves are often thousands of miles across. In the recent display their widest part was reported to be 80,000 miles.

*The reader should, of course, bear in mind that any views advanced which are not yet supported by reliable and repeated experiments are subject to modification, when new evidence is available.*

*Summary.*

It was previously suggested that atomic nuclei and electrons were ejected from the more central part or nucleus of the sun owing to a pressure effect therein. It is now further suggested that some of these particles from the nucleus of the sun escape more or less radially through rifts in the solar envelope (which are the sun-spots) and when these particles enter the earth's atmosphere the aurora is produced in accordance with the ideas of Birkeland and others. The recent sunspot activity, together with the accompanying magnetic storm and aurora, is referred to.

*Notes.*

Referring to my previous paper (*loc. cit.*), the following notes should be associated therewith:—

(*a*) No mention was made of hydrogen in the sun—of course, it is present in considerable quantities.

(*b*) Probably lithium is present in the sun. See A. S. King, *Astrophys. Journ.*, 1916, xliv., 169.

(*c*) The idea of the nuclear parts of atoms coming into conflict due to pressure was discussed. It

is of interest to note C. A. Parsons' (*Inst. of Metals Journ.*, 1918, xx., 5) account of his attempts to produce diamonds. In these trials, a steady pressure of 15,000 atmospheres per sq. inch, with a momentary pressure twenty times as great was obtained, and it was stated to be about one-half that at the centre of the earth, while in many stars the pressure would be enormously greater. This value would be "only a fraction of one-thousandth part of the pressure at the centre of the large stars." In one experiment in which a steel piston was driven by the explosion of powder against a gas charge of oxygen and acetylene contained in a bored steel block, the pressure was supposed to be about 15,000 atmospheres per sq. inch, and the instantaneous temperature reached 17,700° C. (calculated). See in this connection CHEMICAL NEWS, 1921, cxxii., 235: a method proposed by Parsons to reach very high instantaneous pressures.

(*d*) From certain mechanical or kinetic considerations, perhaps it is not correct to consider such enormous pressures, as suggested in the case of the disintegration of atoms in the sun, to act entirely as a displacement blow or shear, and consequently *spin energy*, as it might be termed, may become a factor. Then, in turn, centrifugal force would have to be taken into account. However this may be, besides this latter consideration, the favourable chance positions of the atoms or their nuclei possibly enter into the problem.

*Corrections.*—In my communication on page 169 of this volume, a faulty sentence occurred in the tenth paragraph. It should read: "This experimental work is of very far-reaching significance, and it is especially important in affording a powerful tool for investigating sub-atomic phenomena and revealing secrets which some years ago one would have considered beyond the power of man to discover."

On page 219 of this volume, eighth paragraph, in two places the Greek letter "α" should be inserted before the word -particles. This, of course, was a typographical error.

## THE MECHANISM OF FLOCCULATION IN SOILS.*

By NORMAN M. COMBER, B.Sc., A.R.C.S., A.I.C.

THE texture of a mineral soil is determined by two chief factors, namely, the size of the particles and the arrangement of the particles.

*The size of the ultimate particles* is manifestly permanent and unalterable for all practical purposes. Information regarding this factor is of great importance, and for the purpose of obtaining and expressing such information the soil particles are conventionally graded. In this country it is customary to divide all particles capable of passing a 3-mm. sieve into six "fractions," namely:

| | | Diameter. mm. |
|---|---|---|
| 1. | Gravel ... ... | 3·00—1·00 |
| 2. | Coarse sand ... | 1·00—0·20 |
| 3. | Fine sand ... | 0·20—0·04 |
| 4. | Coarse silt .. | 0·04—0·01 |
| 5. | Fine silt ... ... | 0·01—0·002 |
| 6. | Clay ... ... | below 0·002 |

The finer fractions are separated by sedimentation; the coarser ones by sieving.

*The arrangement of the particles* in a soil is by no means permanent, but is liable to relatively rapid changes. Besides the obvious rearrangement which will be caused by compressing or by loosening the soil, the smallest particles (the fine silt and the clay) become under certain conditions aggregated together to produce what is, in practical effect, a lesser number of larger particles and a consequent lightening of the soil. This aggregation or flocculation process is affected by a number of conditions such as freezing and thawing, sun-drying, and the presence of electrolytes. It is reversible, and deflocculation follows the removal of the factor causing flocculation.

In this paper it is proposed to offer some observations regarding this flocculation process as it is brought about by electrolyte in general, and by lime in particular.

### *The Effect of Fertilisers on Soil Texture.*

It is well established by experience and experiment in the field, that the addition of certain fertilisers has an effect upon the soil texture. Thus, the excessive or prolonged use of nitrate of soda (which has been shown by Hall (see "The Book of the Rothamsted Experiments," 1919, pp. 295-305) and his co-workers to give rise to sodium carbonate in the soil) is known to enhance the stickiness of a soil, and to so deflocculate the clay that it is removed in measurable amount in a turbid drainage water. Laboratory experience abundantly confirms the field observation that small amounts of alkaline substances, such as the carbonates and hydroxides of sodium potassium and ammonium, deflocculate soil clay, giving it the power of remaining in suspension almost indefinitely, making it very difficult to filter, and rendering it extremely sticky when in mass.

By far the most striking and the most important case which arises in agricultural practice is the amelioration of the texture of clay soils which results from the addition of lime. It is established by the experience of many generations that dressings of lime of the order of one to two tons to the acre greatly diminishes the stickiness of a clay soil, reduces the plough draught, and facilitates drainage. The laboratory examination of the subject shows that this action of lime is due to the aggregation or flocculation of the particles.

In farming practice, however, it is not an invariable rule that lime thus improves the texture of all heavy soils. Field experience shows that there is a distinction between heavy soils which respond, in respect of their texture, to dressings of lime and those which do not so respond; and this distinction is found to coincide with that between heavy soils containing a dominant amount of the clay fraction and those whose heaviness is due to a dominant amount of the fine silt fraction. *Clay is readily flocculated by lime, fine silt is not.*

### *The Flocculation of Soils and the Isoelectric Point Theory.*

There have been very many investigations of the power of various electrolytes and colloids to flocculate suspensions of soil particles and of kaolin. In general the results indicate a process analogous to the flocculation of suspensoid sols, and which admits of explanation on the basis of the isoelectric point theory.

*A Contribution to a General Discussion on "Physico-Chemical Problems Relating to the Soil" held by The Faraday Society, on Tuesday, May 31, 1921.

For instance, if a series of similar suspensions of soil particles is treated with colloidal ferric hydroxide in amounts which gradually increase from one end of the series to the other, a point of optimism and immediate flocculation can be found, and amounts of the positive sol greater or less than that producing the optimum flocculation, have less effect. Similar results can be obtained by the use of ferric chloride, aluminium hydroxide, and aluminium chloride (the details of these experiments will shortly be published elsewhere). Such results are analogous to those obtained by Burton in the flocculation of metal sols by aluminium salts (see Burton, "The Physical Properties of Colloidal Solution," 1916).

Again, with electrolytes as flocculants the valency rule is applicable as well to the flocculation of soil suspensions as to that of suspensoid sols. Hall and Morison (*J. Agric. Sci.*, 1907, ii., 244) in a careful investigation of the flocculation of kaolin suspensions certainly failed to elicit the quantitative requirements of Whetham's theory, but they showed quite clearly that the trivalent kations of salts had a flocculating power superior to that of divalent kations which in turn were more effective than monovalent kations.

The flocculation of soil particles appears therefore to fall fairly well into line with the flocculation of suspensoid sols and, with the flocculation of these sols, to be amenable to the isoelectric point theory. There is, however, one well-known exception which happens to be the only case of soil flocculation which is of great practical importance. The flocculation of clay by lime does not appear compatible with the electrical theory, since the hydroxyl ion will, according to the theory, tend to stabilise the suspension.

*The Flocculation of Clay by Lime.*

The explanation of this anomalous case of flocculation which is commonly advanced is that lime added to the soil becomes converted into calcium bicarbonate which latter compound then acts as the flocculant. This explanation is, however, difficult to accept for several reasons of which the following are the chief :—

(1) It affords no explanation of the difference between the action of lime on clay and on fine silt.

(2) If two similar clay suspensions are treated, one with calcium hydroxide and one with calcium bicarbonate in equivalent amount, flocculation is much more rapid in the former case. (The reverse is true of suspensions of fine silt, and, as shown by Hall and Morrison, of kaolin).

The present writer has examined the effect of alkalinity on the flocculation, by calcium salts, of clay and fine silt suspensions (Comber, *J. Agric. Sci.*, 1920, x., 425). It was found that *the flocculation of clay by calcium nitrate is greatly enhanced by the addition of a small amount of ammonium hydroxide, while the flocculation of fine silt by calcium salts is retarded by the addition of alkali.* It must also be noted that the volume of the coagulum is noticeably large when compared with the volume of the coagulum formed by neutral salts.

It seems clear, then, that the flocculation of clay by lime is a genuinely abnormal case in which the hydroxyl ion actually facilitates the action.

*The Mechanism of Flocculation in Soils.*

In endeavouring to find an explanation of clay flocculation in general, and of the abnormal effect of alkalinity upon the flocculation of clay by the calcium ion in particular, it is necessary to bear in mind two important and pertinent facts about clay, namely :—

(1) Clay is very reactive. With solutions of neutral salts it enters into the process of base exchange, and for this reason the flocculating effect of salts is not to be interpreted as necessarily and entirely a direct effect of the kation of the particular salt used. Also, clay is readily susceptible to dissolution by acids, and flocculation by acids will be complicated accordingly.

(2) The clay particle in water does not present a sharp, solid-liquid surface. The relationship of clay to water is different from that of other soil fractions, kaolin and ignited clay (see Keen, *J. Agric. Sci.*, 1920, x., 44), and the peculiarities of clay in this respect strongly indicate that the clay particle is related to the water through the intermediation of organic and siliceous colloidal matter. Unignited soil clay seems to stand apart from other fractions and from kaolin by reason of its marked protection by "emulsoid" material.

Taking cognisance of these two facts about clay—its reactivity and its protection (regarding protection of clay by humus, see Sven Oden, *J. fur handwirt*, 1919, p. 177)—it seems clear that three cases of flocculating action may be possible, namely :—

1. *Direct flocculation* in which the flocculant acts in the same manner as on unprotected and non-reactive suspended particles, the action being merely diminished or delayed by reason of the protection.

There are probably few, if any, cases in which the flocculation of clay is exclusively of this type. The action of iron and aluminium salts and of the colloidal hydroxides of iron and aluminium may be predominantly a direct action. A concentration of these flocculants which produces a maximum effect is easily observable, and in this respect the phenomenon seems to be analogous to the flocculation of metal soils.

2. *Indirect flocculation* in which the products of a previous reaction, such as base exchange or dissolution, act as flocculants.

When neutral salts are used as flocculants it seems assured that the action is to some extent of this second type. There is invariably a partial exchange of kations when neutral salt solutions are in contact with clay, the base exchange process is very rapid, and it appears inevitable therefore that some part of the flocculating action is due to the kations brought into solution from the clay.

The flocculation of clay by acids seems also to be largely indirect and attributable to the action of aluminium, &c., dissolved by the acid from the clay. In the flocculation of kaolin, Hall and Morrison (*loc. cit.*) found that mineral acids were slightly better flocculants than aluminium salts, and suggest that the flocculating power of the latter may be partly due to the acid formed by hydrolysis. With soil clay the case seems to be the reverse of this. Using hydrochloric and aluminium chloride in one set of experiments, and sulphuric acid and aluminium sulphate in another, and using several different clays, the present writer has found that the aluminium salts flocculate soil clay much more rapidly than the corre-

sponding acid in equivalent amount (the details of these experiments will shortly be published elsewhere). It is therefore suggested that the action of acids may to some extent be ascribed to the bases they bring into solution.

3. *Abnormal flocculation* in which the flocculant reacts with the protecting emulsoid matter forming a coagulum which entrains the particles.

This type of clay flocculation seems to be of greatest agricultural importance, for it appears to provide a feasible explanation of the abnormal flocculation of clay by lime, the fact of which has been described above.

When calcium hydroxide is added to a dilute silicic acid sol, a gelatinous precipitate is formed. This precipitate is not formed when a *neutral* calcium salt is added to the neutral sol: it is produced by the action of calcium ions only when the medium of action is alkaline. The precipitate has been investigated by Le Chatelier ("La Silice et les Silicates," 1914), who found that it consisted of silica with varying amounts of lime, and that the lime is easily and entirely removed by washing. Another feature of this precipitate is its enormous volume: according to Le Chatelier 1 grm. of it settles to occupy a volume of 2 litres.

Now if the protection of clay particles is in part due to colloidal silica, which seems certain to be the case, then the addition of lime—the addition of calcium ions and hydroxyl ions—will produce a precipitate such as that described. The production if such a precipitate, entraining the particles seems to be a satisfactory explanation of the flocculation of clay by lime. It accounts for the fact that alkalinity facilitates the flocculation since the formation of the precipitate is dependent upon alkalinity. It accounts for the reversibility of the action since the precipitate is hydrolysed by washing. It accounts for the large volume of the clay coagulum since the precipitate is phenomenally voluminous. Further, this theory of the abnormal flocculation of clay by lime, postulates nothing about clay other than a siliceous emulsoid protection which is already strongly indicated by quite independent considerations.

The effect of small amounts of colloidal silica on the flocculation of finely divided particles in suspension was examined by using a sample of oxide of iron in the form of an impalpable powder. The oxide of iron, when shaken with pure water, did not remain long in suspension, but traces of silicic acid sol gave not only stability to the suspension but also the power of being flocculated by calcium salts much more readily in the presence of alkali than in neutral suspension. It was found in one case that 0·6 mgrms. $S_1O_2$ was able to affect 300 mgrms. of the oxide of iron in this respect. Evidently, therefore, very small amounts of colloidal silica in conjunction with finely divided particles can produce a system susceptible to the abnormal flocculation which is found in the case of clay.

While, then, the mechanism of flocculation in soils does not generally appear to be essentially different from that of the flocculation of suspensoid sols, the flocculation of clay by lime is a process of a distinctly different type. Using the prevalent terminology it is an "emulsoid" phenomenon and is quite out of line with the flocculation of "suspensoids." As an emulsoid phenomenon it appears to be explicable on the basis of the reaction between calcium hydroxide and colloidal silicic acid, and the assumption, which that explanation involves, of a particular colloidal condition which differentiates clay from other soil fractions and from kaolin, is consistent with the peculiarities of clay which have been brought to light by other investigations.

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## THE PURIFICATION AND SOME PHYSICAL PROPERTIES OF CERTAIN ALIPHATIC ALCOHOLS.

By ROGER F. BRUNEL, J. L. CRENSHAW and ELISE TOBIN.

Concluded from 271)

*Iso-Butyl alcohol.*—Boiling point: (1) thermoelement: boiled 4 hours with barium oxide, 107·877°; distilled from barium oxide without long boiling, 107·874-107·888°; aluminum amalgam, 107·881°; (2) obtained by the authors at the Bureau of Standards, 107·89°.

The data for distillation of two specimens follow. A third specimen was worked up from residues

(A) 265 g.: I., below 107·86°, 15 g.; II., 107·86-107·89°, 48 g.; III., 107·89, 170 g. (B) I., 107·88-107·89°, 14 g.; II., 107·89°, 66 g.

Particular attention is called to the densities of this alcohol, seen in the table below. In this case the density is of little value as a criterion of purity.

*sec.-Butyl alcohol.*—Since the thermometers gave concordant values for the boiling point and our supply of this alcohol was limited, it was not tested with the thermoelement. The thermometer readings are especially relable since thy lie so close to the 100° point. (1) Thermometers: 99·52°, 99·53°, 99·53°.

This was one of the alcohols most readily purified. The data in the table below appear to be sufficient.

*Methyl-iso-butyl carbinol*: Aluminum amalgam dries this very slowly, partly, at least, because of the slight reactivity of the drying agent with the alcohol itself. After several hours' boiling a large part of aluminum had still not reacted. In addition to this, the boiling point of the alcohol is so far above 100° that the water has a particular tendency to distil out of the alcohol and collect in the condensed liquid in the cooler parts of the apparatus. It is difficult to prevent this altogether since too prolonged, vigorous boiling causes too much loss of vapour around the ground-glass stopper of the apparatus.

The values obtained were from 131·78° to 131·826°, and the higher value is more likely to be correct. The value obtained at the Bureau of Standards was much too low. The values on our thermometers were also unsatisfactory, varying from 131·77° to 131·85°. The value 131·82° must be nearly correct.

This alcohol was easily purified. A good deal came over within 0·01° on the first distillation, and 72 per cent. of this, on redistillation, came over constantly. This, and other constant boiling portions were distilled as follows:—

(A) wt., 320 g. I., Below 131·79° less than 1 g., total to 131·81°, 12 g.; II., 131·81°, 73 g.; III., 131·81°, 166 g.; IV., 131·81°, 50 g.; II., III., and IV., 289 g.

TABLE I.

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|
| | Const. boiling portion. | | | | | | |
| Specimen | % of total | % of part distd. | $dt/dP$. | B.p. °C. | $d^{25}_{4}$ | $\eta^{D}_{25}$ | $M^{D}_{25}$ |
| | | | Ethyl Alcohol. | | | | |
| | | 100 | 0·035 | 78·32 | 0·78505 | 1·3595 | 12·93 |
| | | | *n*-Propyl Alcohol | | | | |
| A ... ... ... ... ... ... | 56 | 78 | 0·036 | 97·19 | 0·79975 | 1·3833 | — |
| B ... ... ... ... ... ... | 47 | 63 | — | — | 0·79992 | 1·3832 | — |
| Most probable values: | | | | 97·19 | 0·7998 | 1·3833 | 17·54 |
| | | | *Iso*-Propyl Alcohol. | | | | |
| A-III ... ... ... ... ... ... | 84 | 87 | 0·033 | 82·26 | 0·78089 | 1·3750 | — |
| IV. | | | — | — | 0·78167 | 1·3750 | — |
| B ... ... ... ... ... ... | 70 | 81 | — | — | 0·78071 | 1·3749 | — |
| C ... ... ... ... ... ... | — | 57 | — | — | 0·78072 | 1·3748 | — |
| D (Res.) ... .. ... ... | — | 56 | — | — | 0·78086 | 1·3749 | — |
| Most probable values: | | | | 82·26 | 0·7808 | 1·3749 | 17·61 |
| | | | *n*-Butyl Alcohol. | | | | |
| A ... ... ... ... ... ... | — | 90 | 0·036 | 117·71 | 0·80560 | 1·3974 | — |
| B-V. | | | — | — | 0·80566 | 1·3974 | — |
| VI. ... ... ... ... ... ... | 69 | 78 | — | — | 0·80571 | 1·3974 | — |
| VII. | | | — | — | 0·80586 | 1·3973 | — |
| Most probable values: | | | | 117·71 | 0·8057 | 1·3974 | 22·17 |
| | | | *Iso*-Butyl Alcohol. | | | | |
| A .. ... ... ... ... ... | 64 | 73 | 0·036 | 107·89 | 0·79800 | 1·3938 | — |
| B ... ... ... ... ... ... | — | 82 | — | — | 0·79800 | 1·3939 | — |
| C (Res.) ... ... ... ... | 72 | 77 | — | — | 0·79802 | 1·3939 | — |
| Most probable values: | | | | 107·89 | 0·78801 | 1·3939 | 22·21 |
| | | | *sec.*-Butyl Alcohol. | | | | |
| A-III. ... ... ... ... ... | — | — | 0·036 | 99·53 | 0·80270 | 1·39495 | — |
| IV. ... ... ... ... ... | — | over 90 | — | — | 0·80276 | 1·39495 | — |
| B ... ... ... ... ... | 83 | 97 | — | — | 0·80267 | 1·39495 | — |
| Most probable values: | | | | 99·53 | 0·80271 | 1·39495 | 22·1[illegible] |
| | | | Methyl-*iso*-Butyl-carbinol. | | | | |
| A-II. | | | 0·040 | 131·82 | 0·80251a | 1·40895 | — |
| III. ... ... ... ... ... | 88 | 96 | | | 0·80238 | 1·40895 | — |
| IV. .. .. ... ... ... | — | — | — | — | 0·80250 | 1·40885 | — |
| B ... ... ... ... ... | — | 84 | — | — | 0·80243 | 1·40895 | — |
| Most probable values: | | | | 131·82 | 0·825 | 1·40895 | 39·61 |

(a) The fractions of Specimen A were tested in very humid weather. Possibly the values should have been identical.

TABLE II.

| Author. | B.p. °C. | $d^{25}_{4}$ | $\eta^{D}_{25}$ |
|---|---|---|---|
| | Ethyl Alcohol. | | |
| Mendelejeff[1] ... ... ... ... ... ... ... ... ... .. | 78·303 | —— | — |
| Ramsay and Young[2] ... ... .. ... ... ... ... ... | 78·33 | —— | — |
| Noyes and Warfel[3] ... ... ... ... ... ... ... ... | 78·30 | —— | — |
| Andrews[4] ... ... .. ... .. ... ... ... ... ... | — | 0·78510 | 1·35941 |
| Doroshevski and Dvorzhanchik[5] ... ... ... ... | — | —— | (24°) 1·35927 |
| Doroshevski and Polianski[6] ... ... ... ... ... ... | 78·35 | —— | — |
| Wade and Merriman[7] ... .. . ... .. ... .. | 78·39 | —— | — |
| Osborne, McKelvy, and Bearce[8] ... .. . . ... . . | — | 0·78506 | — |
| Robertson and Acree[9] ... ... ... .. ... .. | — | 0·785085 | — |
| Richards and Coombs[10] ... ... ... ... ... ... ... | 78·42 | —— | — |
| Authors' values ... ... ... ... ... ... ... . . | 78·32 | 0·78505 | 1·3595 |
| | *n*-Propyl Alcohol. | | |
| Brühl[11] ... ... ... ... ... ... ... ... ... ... ... | 97·3-·5 | 0·8005 (20°) | 1·3836 |
| Naccari and Pagliani[12] ... ... ... . . ... ... ... | — | 0·8004 | — |
| Perkin[13] ... ... ... ... ... ... ... ... ... ... | 98 | 0·8001 | — |
| Ramsay and Young[14] ... ... ... ... .. ... .. | 97·4 | 0·7995 | — |
| Landolt and Jahn[15] ... ... ... ... ... ... ... ... | 96·1 | 0·8017 (17·8°) | 1·3835 |
| Loomis[16] ... ... ... ... .. ... ... ... .. ... | 97·2 | 0·8000 (20°) | — |
| Young and Fortey[17] ... ... ... . . ... ... | 97·19 | 0·7994 (0°) | — |
| Holmes and Sagemann[18] ... ... ... ... .. ... | 97·2-·4 | 0·79972 | — |
| Doroshevski and Rozhdestvenski[19] .. ... ... ... | 97·26 | 0·7994 (20°) | — |
| Doroshevski and Dvorzhanchik[20] .. ... ... ... | — | —— | (20°) 1·38365 |
| Authors' values ... ... ... ... ... ... ... ... | 97·19 | 0·7998[21] | 1·3833 |

TABLE II. (*continued*).

| | | | |
|---|---|---|---|
| | *iso*-Propyl Alcohol | | |
| Brühl[22] | 82-83 | 0·7844 (20°) | 1·3756 |
| Zander[23] | 82·7-·9 | 0·7794 (17°) | — |
| Perkin[13] | — | 0·78220 | — |
| Thorpe[24] | 81·6-82·1 | 0·7811 (15°) | — |
| Louginine[25] | 82·04 | —— | — |
| Doroshevski | 82·42[26] | 0·7807[27] (20°) | — |
| Doroshevski and Dvorzhanchik[20] | — | —— | 1·37534 |
| Authors' values | 82·26 | 0·7808 | 1·3749 |
| | *n*-Butyl Alcohol. | | |
| Kahlbaum[28] | 117·6° | —— | 1·39747 |
| Doroshevski and Dvorzhanchik[20] | 117·1 | —— | 1·39749 |
| Authors' values | 117·71 | 0·8057 | 1·3974 |
| | *iso*-Butyl Alcohol. | | |
| Perkin[13] | 107·6-8·3° | 0·79852 | – |
| Traube[29] | — | 0·8000 (20°) | — |
| Landolt and Jahn[30] | 107·25 | 0·7987 (17·5°) | 1·3941 |
| Naccari and Pagliani[12] | — | 0·7972 | — |
| Doroshevski and Dvorzhanchik[20] | 107·93 | 0·7976 (15°) | 1·39396 |
| Doroshevski[27] | 107·5 | —— | — |
| Michael and Zeidler[31] | 107·67-·75 | —— | — |
| Richards[32] | 107·2-·3 | —— | — |
| Authors' values | 107·89 | 0·79801[33] | 1·3939 |
| | *sec*.-Butyl Alcohol. | | |
| Pickard and Kenyon[34] | 99° | 0·8039 | — |
| Dogolenko[35] | — | 0·8024-0·8031 (20°) | — |
| Authors' values | 99·53 | 0·80271 | — |

The temperatures in parenthesis are those of the the original determinations, from which the values given were calculated.

*References*.—(1) *Z. Chem.*, 1865, 257. (2) *J. Chem. Soc.*, 1885, xlvii., 654. (3) *J. Amer Chem Soc.*, 1901, xxiii., 465. These authors state that they consider their value probably less reliable than that of Ramsay and Young. (4) *Ibid.*, 1908, xxx., 357. (5) *C.A.*, 1908, ii., 2181. (6) *Z. physik. Chem.*, 1910, lxxiii., 192. (7) *J. Chem. Soc.*, 1911, xlix., 1002. (8) *J. Wash. Acad. Sci.*, 1912, ii., 95. (9) *Am. Chem. J.*, 1913, xlix., 497. (10) *J. Amer. Chem. Soc.*, 1915, xxxvii., 1669. (11) *Ann.*, 1879, cc., 173. (12) *Atti. Accad. Sci. Torino*, 1881, xvi., 407. (13) *J. Chem. Soc.*, 1884, xlv., 466. (14) *Phil. Trans.*, 1889, clxxx., 140. (15) *Z. physik. Chem.*, 1892, x., 288. (16) *Ibid.*, 1900, xxxii., 594. (17) *J. Chem. Soc.*, 1902, lxxxi., 725. (18) *Ibid.*, 1909, xcv., 1936. (19) *J. Russ. Phys. Chem. Soc.*, 1910, xl., 1428. The formula of De Heen, which these authors recommend, was tested by them only between 10° and 20°. When tested by the results of Ramsay and Young, and Naccari and Pagliani for 0°, it is not as satisfactory as the formula of the latter authors, which we have used. (20) *C. A.*, 1909, iii., 1355. (21) Further tests of this value will be made with material now being purified. (22) *Ann.*, 1880, cciii., 12. (23) *Ann.*, 1882, ccxiii., 155. (24) *J. Chem. Soc.*, 1897, lxxi., 923. (25) *Ann. chim. phys.*, 1898, [7] xiii., 307. (26) *Centralbl*, 1911, i., 465. (27) *C. A.*, 1910, iv., 1404. (28) *Z. physik. Chem.*, 1898, xlvi., 628, 646. This author gives $d^{20}_{4}$=0·80978. If we assume the temperature coefficient to be the same as that of *iso*-butyl alcohol, we obtain $d^{25}_{4}$=0·8059. (29) *Ber.*, 1886, xix., 883. (30) *Z. physik. Chem.*, 1892, x., 317. (31) *Ann.*, 1912, cdxciii., 93 (32) *J. Amer. Chem. Soc.*, 1915, xxxvii., 1669. (33) The density appears, in this case, to be easy to duplicate without a high degree of purity. Some years ago one of the authors (*Ber.*, 1911, xliv., 1004) obtained three fractions boiling, altogether, over a range of 0·24°, having densities of 0·79890 to 0·79802. (34) *J. Chem. Soc.*, 1913, ciii., 1940. Value for 25° by linear interpolation. (35) *Z. physik. Chem.*, 1908, lxii., 505. Values estimated from those given for 20° by comparison with Pickard and Kenyon's values.

Another specimen (B) distilled nearly as well. Table I. summarises the distillation data and physical properties of our specimens. Under Col. 2 will be found the per cent of the material taken for the final distillation, which came over at constant temperature. Values are, however, lacking in some cases due to failure to record the total weight before distillation. These values do not fairly represent the purity of the specimens, since they imply that the material remaining in the still would not have come over at the correct temperature, whereas all experiments with these residues indicated that the amount of high boiling impurity in them was small. More significant are the figures in Col. 3, which show the per cent of the amount actually distilled which was collected at constant temperature.

The "most probable values" are not always averages of the results, but are based upon our judgment as to the relative value of the tests or purity of the specimens. We believe the boiling points to be accurate to ±0·01°, except that of methyl - *iso* - butyl - carbinol. The refractivities appear to be accurate to 0·0001. In the case of the densities, however, while the determinations are accurate to 0·00002, the true densities of the substances have not been established, in most cases, nearer than 0·0001.

The values for $dT/dp$ are given in degrees per mm. pressure. The values of the molecular re-

fractivity are calculated according to the equation :

$$M = \frac{\eta^2 - 1}{\eta^2 + 2} \cdot \frac{M}{D}$$

In Table II we have quoted for comparison some of the values to be found in the literature. Among the older values we have included only those which were determined with particular care or which are often quoted. Densities have been recalculated to 25° where they were not determined at this temperature, and we have indicated in parenthesis the temperature of the original determinations in such cases. For alcohols where there is no basis for such calculation, the values are not given.

The reliability of the calculations of the densities is open to question, but the differences between the values are in most cases greater than the possible errors in calculation. The following appear to be the most reliable formulas (the references will be found in the table.

For *n*-propyl alcohol, a formula of Naccari and Pagliani, $d = 0{\cdot}8203 - at + bt^2 - ct^3$ where $\log a = 6{\cdot}90228$, $\log b = 3{\cdot}66482$, $\log c = 2{\cdot}10469$ (−10 after each), and 0·8203 is the density at 0° This equation fits the values of Ramsay and Young (0°, 15°, 25°), Perkin (15°, 25°), Loomis (15°, 20°), and Doroshevski and Rozhdestvenski (10°; 20°), to within 0·0001, after calculation back to a value for d° in each case. (Although the density of the alcohols is affected by slight impurities, the form of the density-temperature curve is apparently not much affected).

For *iso*-propyl alcohol, one of the equations given by Zander, $V_t = V_0\,(1 + 0{\cdot}0010743t + 0{\cdot}06328t^2)$ which very nearly fits the values of Perkin (15°, 25°).

For *iso*-butyl alcohol the equation of Naccari and Pagliani, $d = 0{\cdot}81624 - at - bt^2 - ct^3$ where $\log a = 6{\cdot}87551$, $\log b = 3{\cdot}43912$, $\log c = 1{\cdot}86857$ (−10 after each), and 0·81624 is the density at 0°. This equation fits the values of Perkin (15, 25°) very closely.

The refractivities can be calculated with more certainty, since Doroshevski and Dvorzhanchik showed that the formula $\eta_t = \eta^0/(1 + kt)$ holds for the common alcohols. Where the refractivity has been determined for two temperatures, a value for $k$ can be calculated. We have used for *n*-propyl alcohol, $k = 0{\cdot}032368$ (values of D. and D.); *iso*-propyl alcohol, $0{\cdot}0_32850$ (authors' values); *iso*-butyl alcohol, $0{\cdot}0_3269$ (D. and D.)

No values are given in Table II. for methyl-*iso*-butyl carbinol. It has been prepared by Skita and Ritter (*Ber.*, 1910, xliii., 3397), Pickard and Kenyon (*J. Chem. Soc.*, 1911, xcix , 56), Guerbet (*Compt. Rend.*, 1909, cxlix., 129), and others, but, although its boiling point has been known to be in the neighbourhood of 131°, no determinations of its density or refractivity are recorded.

The authors acknowledge with pleasure the courtesy of the U.S. Bureau of Standards in providing opportunity for the first boiling point tests with one of their resistance thermometers, and, in particular, their indebtedness to Miss Amelia K. Benson, with whose assistance the tests were made.

They also take pleasure in acknowledging their indebtedness to the Warren Fund of the American Academy of Arts and Sciences for a grant which covered the cost of materials for this work, as well as for the preparation of several alcohols on which the work is not yet completed.—*Journal of the American Chemical Society*, March, 1921.

## ELECTRIC OSCILLATIONS ALONG STRAIGHT LINES AND SOLENOIDS.*

By Prof. J. S. TOWNSEND, F.R.S.

A NUMBER of experiments made by the author and Mr. J. H. Morrell to find the relation between the frequencies of the normal oscillations of systems are described.

As in the case of mechanical oscillations, it is necessary to distinguish between a series of free normal modes of oscillation and a series of harmonic oscillations. In the free oscillations of a system having distributed capacity and inductance there is, in general, no exact relation between the frequencies of the different modes of oscillation. A harmonic series of oscillations is obtained in nearly all cases where a fundamental oscillation of constant amplitude is maintained in a system, as, for example, when a tuning fork is maintained in vibration by an interrupted current, or a current is maintained in an oscillatory circuit by a thermionic valve.

The oscillations of solenoids and parallel wires are discussed, and an estimate of the accuracy obtained in measuring wave-lengths by wires is given.

A simple method, depending on harmonic oscillation, is described, whereby the lengths of short waves measured by means of parallel wires may be compared with those of long waves measured by means of standard inductances and capacities.

* Synopsis of Paper read before the Wireless Section of the Institution of Electrical Engineers, June 8, 1921.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

*Ordinary Meeting, June 2. 1921*

PROF. C. S. SHERRINGTON, President, in the Chair

THE BAKERIAN LECTURE was delivered by Dr. T. M. LOWRY, F.R S., and Dr. C. P. AUSTIN, on "*Optical Rotatory Dispersion.*" The following summary was supplied by the Lecturer :—

1. Although no case is known in which Biot's Law of Inverse Squares, $\alpha = k/\lambda^2$, is accurately true, the rotatory dispersion in a very large number of organic compounds can be expressed by the *simple dispersion formula*, $\alpha = k/(\lambda^2 - \lambda_0^2)$, which differs from Biot's formula only in the introduction of a "dispersion constant" $\lambda_0^2$.

2. This simple formula is a special case of the general formula $\alpha = \Sigma k_n/(\lambda^2 - \lambda_n^2)$, introduced by Drude as an approximation based upon the electronic theory of radiation and absorption of light. Substances which require more than one term of this equation are said to show *complex rotatory dispersion.*

3. Tartaric acid and its esters give dispersion curves which frequently show (i.) an inflexion, (ii.) a maximum, (iii.) a change of sign, and are then described as cases of *anomalous rotatory*

dispersion. These can be represented by two terms of Drude's equation :—

$$\alpha = \frac{\lambda^2-\lambda_1^2}{k_1} - \frac{\lambda^2-\lambda_2^2}{k_2}$$

The anomalies mentioned above only appear (i) when the two terms are opposite in sign; (ii) when $k_1>k_2$, if $\lambda_2^2>\lambda_1^2$ The wave-lengths at which the reversal, maximum and inflexion occur are given by

$$\frac{k_1}{k_2}\sqrt{\frac{k_1}{k_2}},\ \text{and}\ \sqrt{\frac{k_1}{k_2}} = \frac{\lambda^2-\lambda_1^2}{\lambda^2-\lambda_2^2}$$

4. The rotatory dispersion in quartz was represented by Drude by a two-term equation, in which the dispersion-constant of the negative term was negligible, so that

$$\alpha = \frac{k_1}{\lambda^2-\lambda_1^2} - \frac{k}{\lambda^2}$$

where $\lambda_1^2=0{\cdot}010627$, $k_1=12{\cdot}200$, and $k=5{\cdot}046$. Since $k_1>k$, the dispersion-curve is complex but not anomalous. In order to express the most recent measurements, it is necessary to assume finite values for both dispersion-constants, and to introduce a term to express the influence of the infra-red absorptions; the infra-red term is, however, very small and can be taken as a constant, so that

$$\alpha = -k + \frac{k_1}{\lambda^2-\lambda_1^2} - \frac{k_2}{\lambda^2-\lambda_2^2}$$

where $\lambda_1^2=0{\cdot}012742$, $\lambda_2^2=0{\cdot}000974$
$k=-0{\cdot}1915$, $k_1=9{\cdot}5644$, $k_2=-2{\cdot}3114$

5. The anomalous dispersion of tartaric acid was attributed by Arndtsen in 1858 to the presence of two modifications of the acid differing in the sign of their rotations and in the magnitude of their dispersions. This view has been confirmed (i) by the proof that the complex rotatory dispersion of the acid and its derivatives can be expressed as the sum of two simple dispersions; (ii) by the discovery of certain "fixed" derivatives of tartaric acid which exhibit simple rotatory dispersion. Attention is directed to some analogies between tartaric acid and nitrocamphor, which gives two isomeric compounds in solution.

## PHYSICAL SOCIETY.

*May 27, 1921.*

PROF. SIR W. H. BRAGG, F.R.S., President, in the Chair.

A paper *"On the Reflection of the X-ray Spectrum of Palladium from Fluorspar,"* was read by Mr. H. PEALING.

An examination of the odd order spectra reflected from the 100 plane of fluorspar, using palladium X-rays has been made with a view to test the Lewis-Langmuir theory of the motion of valency electrons in compounds. Evidence, in partial confirmation of the theory, has been obtained.

DISCUSSION.

Prof. BRAGG said that the relatively high magnitude of the third order spectrum was most curious. There was evidently something diffracting strongly about a third of the way between the calcium and fluorine atoms: it was possibly only a coincidence, but this was where the junction of these atoms occurred.

Prof. RANKINE asked what was supposed to be the source of the diffraction, the nucleus or the electrons distributed round it. If the latter, what was the justification for assuming the diffraction to originate from the planes containing the nuclei?

Prof. BRAGG said the origin of the diffraction was what they were all trying to settle. Possibly the paper he was just about to read would answer Prof. Rankine's question.

Dr. HOPWOOD was not clear as to what the paper proved. Assuming the reflecting power of the calcium and fluorine atoms to be proportional to the atomic numbers the same magnitude for the faint spectra was apparently to be expected with or without the transference of electrons of the Lewis-Langmuir theory. This being so, he did not see that the result was evidence one way or the other.

Mr. PEALING said the discrepancy of the larger third order spectrum was more easily accounted for on the basis of the Lewis-Langmuir theory.

Dr. HOPWOOD thought this might be due to a single distortion rather than to a transfer of electrons from the calcium to the fluorine.

A paper on *"The Intensity of X-ray Reflection by Diamond,"* was read by Sir W. H. BRAGG.

The paper describes an investigation of the relative intensities of the reflections of monochromatic X-rays by the various crystallographic planes of diamond. The special difficulties due to the small size of available crystals and the modification of the usual method required to obviate them are discussed. An interesting feature of the results is that they lie very closely on smooth curves, which indicates that if the outer electrons of the carbon atom lie at any considerable distance from the centre they must be in motion over a wide range, or for some other reason must contribute little to the reflection.

It is shown that the properties of the carbon atom in diamond are based on a tetrahedral and not a spherical form. The tetrahedra point away from any (111) plane in the case of half the atoms, and towards it in the case of the other half. Consecutive 111 planes are not exactly of the same nature and consequently some slight second order reflection from the tetrahedral plane might be expected. This effect, though slight, has been found.

DISCUSSION.

Dr. ANDRADE asked if surface tension effects entered into the problem.

Dr. RAYNER asked if there was any chance of obtaining the arrangement of carbon atoms in the benzene ring.

Prof. BRAGG explained that surface tension effects did not come in. In reply to Dr. Rayner, he exhibited a model of the benzene group.

*Exhibit of Photographs by M. le Duc de Broglie.*

Prof BRAGG exhibited and explained photographs by M. le Duc de Broglie of the "Magnetic Spectra" obtained when the $\beta$-rays produced when X-rays strike copper are deflected on to a photographic plate by a magnetic field.

A paper entitled *"A Method for the Micro-analysis of Gases by the Use of the Pirani Pressure Gauge,"* by the Research Staff of the General Electric Co., Ltd., was read by Dr. N. R. CAMPBELL.

SUMMARY.

(1) A method of analysis of gases at a pressure between 0·61 and 0·001 mm. is described, based on the characteristic vapour-pressure temperature curve of any substance.

(2) The method demands a gauge which will measure the pressures of vapours, as well as of permanent gases, over the range mentioned. The Pirani gauge is suitable for this purpose, especially if it is used in a way which is not new, but of which the advantages have not been sufficiently recognised.

DISCUSSION.

Dr. J. S. G. THOMAS asked if the method would discriminate between the higher hydrocarbons in coal gas, or between ethane and methane It was assumed that the heat lost by conduction at the ends of the supports was constant. He did not think this was justified, as it had been shown that at low pressures this loss depended on the pressure of the gas. Would the method discriminate between dry and wet gas at the same total pressure?

Dr. D. OWEN expressed his admiration of the method, which appeared to be entirely new. To what pressures had the author gone down to in these experiments? In addition to the Pirani gauge the McLeod gauge is referred to, but no others. Had Dr. Campbell any experience of other forms of low-pressure gauge and their properties?

Dr. CAMPBELL, in reply, said it was easy to analyse any mixture of components which could be frozen out by liquid air. They had analysed the vapours from the oil used in their pumps, and he thought the higher hydrocarbons in coal gas would present no difficulty. He was afraid neither ethane nor methane would freeze out, and so could not be treated by this method. As regards the validity of the assumptions of the heat loss for accurate work every gauge is separately calibrated, and no assumptions are made. The instrument could be used to discriminate between wet and dry gas, provided the total pressure is under 0·2 mm. He did not know how low pressures the Pirani gauge would do for, but for very low pressures the Ionisation gauge would be more accurate

## NOTES.

LACQUERS, ENAMELS, VARNISHES.—The manufactures of the New Explosives Company are gaining very great appreciation in all industries. The manufacture of nitrocellulose for industrial purposes has been seriously undertaken by the Company at their Stowmarket factory, and a large number of lacquers and varnishes have been produced. We have had an opportunity of testing several of these productions, and have been particularly interested in the black anti-corrosive enamels, in view of their use in places where heat and noxious fumes are present. The results of tests extending over some months show them to be very valuable; they are easily applied, dry quickly, and keep their surface under conditions where most other paints fail. For "spraying" they are most useful; the dead black particularly gives a fine surface for ironwork that is exposed to acid fumes, such as are met with in the chemical laboratory, while for art ironwork it cannot be surpassed.

TENDERS FOR DISINFECTANTS.—The Ministry of Communications, Belgrade, is inviting tenders to be submitted by June 22 for the supply of the following disinfecting materials: 40,000 kilos. of pink chloride powder (without iron supplements, and without free chlorohydrogen acid); 700,000 kilos. of creosote (with the following specifications—minimum 5 per cent of phenol, cresol, and their "homologues"; it should be liquid at 15° C.). In the offers, which must bear a 10 dinars duty stamp, prices must be stated all charges paid Belgrade or port. They must be enclosed in a sealed envelope, and addressed "Ekonomsk Odelenje, Ministarstva Saobracaja." On the envelope should be written "Ponuda za licitaciju pinkhlorida i creozota." A deposit of 10 per cent by S.C.S. subjects, and 20 per cent by foreigners must be made before or on the date of tendering. It is desirable for United Kingdom firms interested in Serb, Croat, Slovene State contracts to be represented in that kingdom. The Department of Overseas Trade is prepared to assist in the appointment of agents.

BRITISH SCIENCE GUILD.- SUB-COMMITTEE ON APPARATUS.—The question of the quality, supply, and prices of British laboratory glassware, porcelain, and chemicals, including research chemicals, is under consideration by a Committee of the British Science Guild. The Committee, the Chairman of which is Sir. Richard Gregory, is anxious, in view of the conflicting statements which have appeared from time to time on these matters, to obtain the views of scientific workers who have experience of recent articles of the kind described, both of British and foreign manufacture. It is obvious that the information can be of use only when it applies to goods of definitely known origin. The points on which information is desired are: the quality of the goods; their price as compared with that of imported articles of the same quality; the facilities for obtaining supplies; and the effects, if any, on research work of restrictions imposed on the importation of German goods. The Committee would also welcome statements made, or reasoned conclusions arrived at, by competent bodies who have investigated these questions recently, and from manufacturers who wish to add any further definite information to that which has already appeared in the Press. The information should be sent to the Secretaries of the Committee, Prof. J. R. Partington, East London College, or Mr. C. L. Bryant, 23, Peterborough Road, Harrow, as soon as possible.

METRIC SYSTEM ADOPTED IN JAPAN.—The new Weight and Measure Law as passed by the Diet was formally promulgated recently by the Japanese Government, thus rendering Japan one of the metric countries. Simultaneously with the promulgation of the new law, Director Kitsukawa, of the Weight and Measure Office, gave out a statement, saying that even when the first weight and measure law was framed in 1893, Japan was desirous of adopting the metric system, but the nation was not ready to accept it, and the old systems were fully adopted. "Several times since, the wholesale reform of the weight and measure

systems has been attempted," the official's statement continues, "but it was quite difficult, before the war, to break with the old systems and adopt the new one to which the nation was but little accustomed. When the world war started, however, the necessity of adopting the metric system was keenly felt, and the Government Bill was readily accepted by the Diet." According to the Yokohama Chamber of Commerce *Journal*, within the five years beginning with the date from which the Law takes effect, all public works, Government offices, schools, and large factories will be made to adopt the new system, while the general public will be given 20 years' grace.

ACTION OF HIGH TEMPERATURES ON PARAFFIN.—Crude Boryslaw petroleum (d. 0·856) was distilled by Messrs. Burstyn and W. Jakubowicz, after treatment with 50 per cent sulpuric acid (98 per cent at 40° C.), followed by washing. Accordingly as distillation is stopped at 150°, 200°, 250°, or 300° C., the proportion of paraffin obtained in the residue is 13·8 per cent, 12·8 per cent, 12·2 per cent, or 10·1 per cent. In any case the solidification point of the paraffin is 51·5° C. As there are not appreciable quantities of paraffin in the distillates, the differences in the amounts obtained are ascribed to the decomposition even at 125° C., due chiefly to the action of the air. For this reason distillation in a vacuum is recommended.—*Matières Grasses*, April 15, 1921.

ITALIAN MERCURY INDUSTRY.—Monte-Amiata in Grosseto Sierra is the centre of the Italian mercury industry, the production of this district, about 1000 metric tons of metal yearly, representing about the total for all Italy. It is estimated that this deposit can supply ore in much the same quantity for several hundreds of years. The ore-producing zone is 40 kilometres long, running parallel to the Apennines, and covering an area of about 400 sq. kilometres. There are eight mines now worked. The ore is usually red sulphide or cinnabar. The high cost of fuel (coal and wood) is the greatest burden in expenses for smelting. Ther are two types of furnaces in use, one for large pieces of ore, which are mixed with wood fuel, simple shaft furnaces, and the other a special type for smaller pieces. There are two causes which considerably affect cost price, viz., emanations of sulphuretted hydrogen, involving employment of powerful electric fans, and the nature of the soil which becomes saturated with water and causes falls of earth in the galleries.—*Génie Civil*, April 9, 1921.

AN International Agricultural and Industrial Exhibition will be held at Riga from July 31 to August 28, 1921. The Exhibition will be undei the control of the Lettish Government. Full particulars and information can be obtained from The British and Russian Transport Co., Ltd., 6, Lloyd's Avenue, E.C.3.

## BOOKS RECEIVED.

"The Chemical Effects of Alpha Particles and Electrons." By SAMUEL C. LIND. Pp. 182 New York: The Chemical Catalog. Co.

"A Text-book of Inorganic Chemistry" Edited by J. NEWTON FRIEND Vol. IX. Part II., "Iron and its Compounds." Pp.xxv +265 illustrated. London: Charles Griffin & Co. Price 18s. net

"Perfumes, Essential Oils, and Fruit Essences." By GEOFFREY MARTIN. Pp. vii.+138. London. Crosby Lockwood & Sons. Price 12s. 6d net.

## New Patents.

THIS List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W C 2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

14852—Budd, C. C. L. G—Manufacture of hydro-oxycellulose, a new xanthogenated compound therefrom, etc May 28th.

14459—Casale, L.—Apparatus for catalytic synthesis of ammonia. May 24th.

*Specification published this Week.*

163162—Ellis, G. B.—Purification of ammonia salts.

*Abstract Published this Week.*

*Aluminum Sulphate.*—Some further improvements in the process of obtaining Aluminium Sulphate has been Patented No. 161606 by Messrs. Spence & Sons, Ltd., of Alum Works, Holland Street, Manchester. Impure basic aluminium sulphate solutions, obtained by treating ground aluminous material with sulphuric, are freed from iron by agitating with potassium sulphate in the presence of the suspended undissolved material. The invention consists in adding specially prepared finely-divided insoluble matter called "nucleus material" to the substantially clear aluminium sulphate solution containing a potassium salt, before agitating. The insoluble siliceous residue from the treatment of the finely-ground aluminous material with sulphuric acid when re-ground in the wet condition is suitable as nucleus material but finely divided native alunite or other insoluble substances may also be used. It is added in the form of mud either at once or in portions as the purification proceeds. A portion of the separated solids may be used as nucleus material, after further regrinding, in the next operation and valuable constituents are recovered from the remainder, for example by treating with sulphuric acid, preferably after the content of precipitated matter had been raised by repeated use.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

## MEETINGS FOR THE WEEK.

*Tuesday, June 21.*

Mineralogical Society, 5.30.

*Thursday, June 23.*

Royal Society. "A Study of Catalytic Actions at solid Surfaces," by E. F. Armstrong and T P. Hilditch "A Contribution to the Thermodynamical Theory of Explosions": Part I; by Sir J. B Henderson; and Part II (with Prof. H. R. Hassé); "Eddy Current Losses in Cylindrical Conductors with special Applications to the Alternating Current Resistances of short Coils," by S. Butterworth. "On the Currents induced in a Cable by the Passage of a Mass of magnetic Material over it," by E. S. Bieler. "The Experimental Analysis of Sound in Air and Water, some Experiments towards a Sound Spectrum," by Guy Barlow and H. B. Keene. "The Theory of Analysis of an Electric Current by periodic Interruption," by Guy Barlow.

*Friday, June 24.*

Physical Society, 5.

## NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemical Apparatus, &c., for review or notice to be addressed to the EDITOR

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# THE CHEMICAL NEWS.

VOL. CXXII, No 3193.

## EDITORIAL.

AFTER much discussion and enquiry it has been decided to make an alteration in the appearance and also the title and contents of the CHEMICAL NEWS.

The needs of the advertisers have called for a better surfaced paper for the cover, and it has been thought that a distinctive colour will be more satisfactory than the present one, which has remained unchanged since the first issue in 1859.

The great advances that have, within the last 25 years, been made in the domains both of chemistry and physics, and the fact that these advances have been largely absorbed in our national industries has brought the CHEMICAL NEWS into the hands of manufacturers and merchants to a very much greater extent than in the past.

We are, therefore, venturing to alter the latter part of the title to "Journal of Industrial Science" and to make an appropriate alteration to the title-page of the volume.

These are matters of small moment. What is of more importance is that we propose for the future to make the first issue in each month four pages larger than heretofore, and to devote the four additional pages to the notice of the very numerous new books that are now appearing, dealing with chemical and physical science.

Firmly believing that we shall before long enter upon a period when the present state of unrest and agitation will give place to one of serious work and production, it is our intention to lose no time in contributing our mite to the increasing activity in industrial science. We shall greatly value any suggestions and criticisms upon the course we are taking.

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The last Friday Evening Lecture of the Session at the Royal Institution was delivered by Sir J. J. Thomson, O.M., on the "Constitution of the Atom." The subject is one of fascinating interest, and will probably mark an epoch in our accepted ideas of the physical nature of atomic matter. It was pointed out that the recent discoveries of radioactivity had brought the chemist and physicist into very close relation, to their mutual advantage; certainly the old idea of a solid individual particle has gone, and in its place we have an atom of positive electricity surrounded by a more or less complicated system of negative electrons. This idea, originating in the investigations of Sir Ernest Rutherford, Prof. Soddy, and others, has been elaborated by Sir Joseph Thomson, and now stands upon an unassailable foundation. By means of a series of ingenious models and diagrams, the details of the new system were explained, and many of the well-known chemical reactions were made clear.

At the conclusion of the lecture the opportunity was taken to make a presentation to Sir James and Lady Dewar on the occasion of their golden wedding. The gift of the members of the Royal Institution took the form of a very beautifully figured gold vase, and was presented by His Grace The Duke of Northumberland, who briefly reviewed the work of Sir James Dewar, and dwelt upon its world-wide value and importance.

Sir James Dewar, who was visibly affected by the occasion, acknowledged the gift on the part of Lady Dewar and himself, and gave a short history of his long connection with the Institution, and of the vicissitudes through which it had passed.

To the writer, whose acquaintance with the Royal Institution has been of very many years standing, the occasion was one of deep interest. Every detail of the work of Sir James Dewar from the far-away days when the vacuum vessel was a square-sided box of glass, past the early days of the compression of oxygen in brass pumps, through the brilliant researches and the glorious experiments that recorded the liquefaction of air, nitrogen, oxygen, and the inert gases of the atmosphere, passed through the mind in luminous succession, together with the faces of many who at one time seemed to be part of the Institution—now, alas! alive only in remembrance. One or two only are left, and the most prominent of these was Sir James, who occupied the same seat that he always holds (it is unthinkable to imagine him in any other part of the theatre), and it was a real pleasure to hear him speak of continued vigour and hope of further activity: a hope that we heartily endorse.

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## POLYMERISATION AMONGST LIQUIDS.

By WILLIAM R. FIELDING, M.A., M.Sc., Vict.
Senior Science Master at King Edward VII School, Lytham.

IN a previous article (CHEMICAL NEWS, vol. cxxii., No. 3170), I calculated the degree of polymerisation ($p$) for a number of elements and compounds in the solid state. In the present article I propose to find the relative sizes of the aggregations of certain substances at their boiling-points, and then to calculate $p$ for a number of typical liquids.

Assuming the truth of

$$p_x = \frac{k}{W_x S_x}$$

I first made a comparison between the rates of polymerisation of certain liquids at 302° A. For bromine, if W=80, $s$=0·1071, and $p$=1, then $k$=8·57. The results are given in Table I.

TABLE I.

| Substance | W | S. | Relative value of $p$ | Minimum value of $p$ |
|---|---|---|---|---|
| Br ... | 80 | 0·1071 | 1 | 1·37 |
| $H_2O$ ... | 6 | 1 | 1·43 | 1·96 |
| P (yellow) | 31 | 0·2045 at 346° | | |
| | | <0·2045 – F.P. | >1·35 | >1·85 |
| Pb .. | 207 | 0·047 – 653° | | |
| | | <0·047 – F.P. | >0·88 | >1·20 |
| Hg ... | 200 | 0·0333 | 1·3 | 1·78 |
| Cl ... | 35·5 | 0·223 – 240° | | |
| | | >0·223 – 302° | <1·07 | <1·46 |
| Ga ... | 69·9 | 0·0802 – 392 | | |
| | | <0·0802 – F.P. | >1·52 | >2·08 |
| Al ... | 27 | 0·3914 – 947° | | |
| | | <0·39 – F.P. | >0·816 | >1·12 |
| Cu .. | 63·5 | 0·1556 – 1357° | | |
| | | <0·1556 – F.P. | >0·87 | >1·2 |
| Ag ... | 108 | 0·0748 – 1276° | | |
| | | <0·0748 – F.P. | >1·06 | >1·45 |

| | | | | |
|---|---|---|---|---|
| Bi ... | 208 | 0·0363–603° | | |
| | | <0·0363–F.P. | >1·13 | >1·55 |
| Zn ... | 65·4 | 0·1786–732° | | |
| | | <0·1786–F.P. | >0·73 | >1 |
| Sn ... | 119 | 0·0637–513° | | |
| | | <0·0637–F.P. | >1·13 | >1·55 |
| AgCl | 71·7 | 0·129 –767° | | |
| | | <0·129 –F.P. | >0·92 | >1·26 |
| AgBr | 94 | 0·076 –769° | | |
| | | <0·076 –F.P. | >1·2 | >1·64 |
| $PbBr_2$ | 122 | 0·078 –811° | | |
| | | <0·078 –F.P. | >0·9 | >1·23 |
| $PbI_2$ | 154 | 0·0645–648° | | |
| | | <0·0645–F.P. | >0·86 | >1·18 |
| $LiNO_3$ | 23 | 0·390 –549° | | |
| | | <0·390 –F.P. | >0·95 | >1·3 |
| $NaNO_3$ | 17 | 0·430 –623° | | |
| | | <0·430 –F.P. | >1·17 | >1·6 |
| $KNO_3$ | 20 | 0·333 –633° | | |
| | | <0·333 –F.P. | >1·28 | >1·75 |
| $AgNO_3$ | 34 | 0·187 –518° | | |
| | | <0·187 –F.P. | >1·35 | >1·85 |
| $KClO_3$ | 24·5 | 0·325 –550° | | |
| | | <0·325 –F.P. | >1·07 | >1·46 |
| $C_2H_5OH$ | 9·1 | 0·648 | 2·6 | 3·56 |

Raising the least value of $p$ (*i.e.*, 0·73 for zinc) to 1, we obtain the minimum values at 302° A. (last column). Even these values may not be high enough, for $p$ for *every* liquid must be at least 1 at the boiling-point.

In Table II. I have compared the values of $p$ in the solid and liquid states.

TABLE II.

| Substance | Solid. $p$ | Temp. | Liquid. $p$ | Temp. |
|---|---|---|---|---|
| Cl ... ... | 1·5 | 172° | 1·37 | 240° |
| Br ... ... | 1·5 | 266° | 1·37 | 302° |
| P ... ... | 1·53 | 298° | >1·85 | F.P. |
| Bi ... ... | 1·51 | 307° | >1·55 | ,, |
| Sn ... ... | 1·5 | 323° | >1·55 | ,, |
| Pb ... ... | 1·47 | 307° | >1·20 | ,, |
| Al ... ... | 1·72 | 300° | >1·12 | ,, |
| Ga ... ... | 1·71 | 291° | >2·08 | ,, |
| Zn ... ... | 1·58 | 306° | >1 | ,, |
| Hg ... ... | 1·45 | 214° | 1·78 | ,, |
| Cu ... ... | 1·67 | 330° | >1·2 | ,, |
| Ag ... ... | 1·62 | 400° | >1·45 | ,, |
| AgCl ... | 1·48 | 330° | >1·26 | ,, |
| $AgNO_3$ ... | 2·00 | 330° | >1·85 | ,, |
| $NaNO_3$ ... | 2·15 | 316° | >1·6 | ,, |
| $KNO_3$ ... | 2·04 | 303° | >1·75 | ,, |
| $KClO_3$ ... | 2·01 | 307° | >1·46 | ,, |
| $H_2O$ ... ... | 3 | 273° | 1·96 | ,, |

There are at least five elements in this list which are more highly polymerised (at the melting-point) in the liquid than in the solid state, viz., phosphorus, bismuth, gallium, mercury, and tin. (If data were available probably there would prove to be many more). Now mercury and phosphorus contract on freezing; so do copper, lead, tin, silver, &c.; whereas bismuth expands on freezing, like water (see Roberts-Austen: "Introduction to the Study of Metallurgy," 5th edition, p. 16). Hence the difficulty of explaining the phenomenon. It is probable that solid phosphorus consists of monatomic and diatomic molecules, and when liquefaction takes place, some of the phosphorus molecules associate to form $P_2$, $P_4$, &c., molecules. The same explanation might apply to bismuth, gallium, mercury, &c (see further reference to this subject after Table VI.).

As I wished to compare the degree of polymerisation of different groups of compounds between 200-400° A., I tried to select two elements which are liquid within these limits, in the same group of the Periodic Table, if possible, so that I could assume with some justification that they acted somewhat similarly, *i.e.*, either aggregated or polymerised to the same extent at corresponding temperatures.

Assuming $p=1·37$ for bromine at 302° A., then it is $<1·46$ for chlorine at 302° A., but $>< 1·46$, *i.e.*, about 1·37 at 240° A. I made the bromine aggregation at 302° = 2, *i.e.*, its vapicular weight is 160. Then,

$$\frac{T \times p \times s \text{ (observed)}}{R_T} = k$$

Substituting 302° A. for T,
1·37 for $p$,
0·1071 for $s$ at 302°,
2 for $R_T$ ——,
then $k=22·15$.

For chlorine (at 240° A.) $R_T=3·31$, and its vapicular weight = 118. Thus,

| | Cl | Br |
|---|---|---|
| T ... ... ... ... ... ... | 240 | 302 |
| Vap. wt. ... . . ... ... | 118 | 160 |

By inter- and extra-polation the vapicular weights corresponding to all temperatures quoted in this paper can readily be obtained (1° rise or fall in temperature = 0·68 in V. wt.). Or a formula, similar to that used for solids, connecting vapicular weights and temperature, can be obtained as follows:—

$$\frac{240-x}{\sqrt{118}} = \frac{302-x}{\sqrt{160}}$$

$$x = -136$$

$$\therefore \frac{T+136}{\sqrt{\text{Vap. wt.}}} = k$$

From data for chlorine,

$$\frac{240+136}{10·86} = k = 34·62$$

$$\therefore \frac{T+136}{34·62} = \sqrt{\text{Vapicular weight}}$$

The results for water are given in Table III. The specific heats used are those obtained by Callender and Barnes (quoted in Edser's Heat). There are several tables given in Landolt-Börnstein, "Physikalisch-Chemische Tabellen," but they are all slightly different from each other, agreeing only in one respect, that the minimum specific heat is between 293° and 313° A.

TABLE III.

| Absolute Temp. | | $S_T$ | $S_{obs}$ | $p$ |
|---|---|---|---|---|
| 273 (ice) | (R=69) | — | — | 3 |
| 273 | ($R_1$=23·3) | 1·8904 | 1·0054 | 1·88 |
| 283 | | 1·9175 | 1·0022 | 1·91 |
| 293 | | 1·93 | 1·0000 | 1·93 |
| 303 | | 1·9591 | 0·9987 | 1·96 |
| 313 | | 1·9673 | 0·9982 | 1·97 |
| 323 | | 1·9887 | 0·9987 | 1·99 |
| 333 | | 2·0090 | 1·0000 | 2·01 |
| 348 | | 2·0240 | 1·0024 | 2·02 |
| 363 | | 2·0441 | 1·0053 | 2·03 |
| 373 | | 2·0606 | 1·0074 | 2·04 |

Thus, throughout the liquid state there is a slight rise in the value of $p$. On melting, apparently, some of the trihydrol breaks up into dihydrol and monhydrol. Consider 100 molecules of trihydrol. Let $x$ persist when the ice melts, the remaining $(100-x)$ molecules breaking up into $(100-x)$ molecules of dihydrol, and $(100-x)$ molecules of monhydrol. There are now $(200-x)$ molecules of tri-, di-, and monhydrol present, whose average degree of polymerisation is 1·88.

$$\therefore\ 1{\cdot}88\ (200-x)=100\times 3$$
$$\therefore\ x=40{\cdot}4$$

Thus, 59·6 per cent of the trihydrol breaks up when ice is melted, and of the new molecules formed 40·4 are $(H_2O)_3$, 59·6 are $(H_2O)_2$, and 59·6 are $(H_2O)$. That is, there is an increase in the number of molecules, yet a decided diminution in volume. Thus, at 273° A., water contains 40·4 per cent by *weight* of trihydrol, and *by number* 25·3 per cent of $(H_2O)_3$, 37·3 per cent of $(H_2O)_2$, and 37·3 per cent of $H_2O$.

This is assuming that none of the monhydrol molecules associate amongst themselves to form dihydrol. Supposing all the monhydiol becomes dihydrol, then the equation becomes

$$1{\cdot}88\left\{\frac{300-x}{2}\right\}=300,$$

which gives a negative value for $x$. From Table III. it will be obvious that the monhydrol molecules could not all be transformed into dihydrol until above 330° A. (when $p=2+$) although a certain proportion may do so at any temperature between 273° and 373° A. That something like this is occurring is evident from the irregular specific heats, and from the fact that the point of maximum density can be lowered by increasing the pressure, when $p$ would be altered too.

The three kinds of molecules exist side by side, in varying amounts, until boiling-point, when liquid water is about two-thirds dihydrol (see Table IV.). At the conversion of 100 molcules of trihydrol (ice at 273° A.) into 159 mixed molecules at the same temperature, there is a decided shrinkage in volume, showing that trihydrol has a big configuration, and monhydrol a small one, the dihydrol coming in between. Under increased pressure, ice (at 273° A.) liquefies, its volume is reduced, and presumably the bulky trihydrol configurations are broken down, thereby reducing the value of $p$. The relation between pressure and $p$ will be dealt with later.

The specific heat of trihydrol (ice at 273° A.) $= \dfrac{9}{6\times 3} = 0{\cdot}504$.

The specific heat of dihydrol $= \dfrac{11{\cdot}34}{W\times p} = 0{\cdot}945$ (at 273° A.).

The specific heat of monhydrol $= \dfrac{11{\cdot}34}{W\times p} = 1{\cdot}890$ (at 273° A.).

I have calculated the relative sizes of these three molecules as follows: I have assumed that the size of the dihydrol molecule is the arithmetical mean of the other two.

Let size of trihydrol molecule be 2; then size of dihydrol molecule is $1+x$; and size of monhydrol molecule is $2x$. 11 cc. of ice at 273 become 10 cc. of water at the same temperature. Therefore, starting with 100 molecules of trihydrol,

$$100\times 2=\tfrac{11}{10}\left\{(40{\cdot}4\times 2)+59{\cdot}6(1+x)+59{\cdot}6(2x)\right\}$$
$$=\tfrac{11}{10}(80{\cdot}8+59{\cdot}6+59{\cdot}6x+119{\cdot}2x)$$
$$=\tfrac{11}{10}(140{\cdot}4+178{\cdot}8x)$$
$$\therefore\ x=0{\cdot}231$$
$$\therefore\ 2x=0{\cdot}462$$
$$\therefore\ 1+x=1{\cdot}231$$

The relative volumes are:—

$$\left.\begin{matrix}(H_2O)_3 & 2\\ (H_2O)_2 & 1{\cdot}231\\ (H_2O) & 0{\cdot}462\end{matrix}\right\}\ \text{or}\ \left.\begin{matrix}4{\cdot}33+\\ 2{\cdot}66+\\ 1\end{matrix}\right\}$$

Their relative densities can be obtained as follows:—

| | Relative number at 273° A | Relative Vols. | Relative Weights | Relative Densities |
|---|---|---|---|---|
| $(H_2O)_3$ ... ... | 40·4 | 2 | 3 | 1·5 |
| $(H_2O)_2$ ... .. | 59·6 | 1·231 | 2 | 1·624 |
| $(H_2O)$ ... ... | 59·6 | 0·462 | 1 | 2·164 |

Total volume $=140{\cdot}4+178{\cdot}8\ x$ (where $x=0{\cdot}231$)
$=181{\cdot}7$

Total weight $=300$

$$\therefore\ \text{Density}=\frac{300}{181{\cdot}7}=1{\cdot}651$$

The actual density of water at 273° A. is 1, so that the densities of $(H_2O)_3$, $(H_2O)_2$, and $(H_2O)$ are 0·908, 0·983, and 1·310 respectively.

What happens to water at 4° C.?

Let $m$ additional molecules of trihydrol break up between 273° and 277° A., and further, assume that none of the monhydrol is transformed into dihydrol. The water formed at 273° has a volume of $140{\cdot}4+178{\cdot}8x=181{\cdot}7$.

The volume at 277° A. (4° C.) will be

$$2(40{\cdot}4-m)+1{\cdot}231(59{\cdot}6+m)+0{\cdot}462(59{\cdot}6+m)$$
$$=(80{\cdot}8-2m)+(73{\cdot}4+1{\cdot}231m)+(27{\cdot}5+0{\cdot}462m)$$
$$=181{\cdot}7-0{\cdot}307m.$$

$$\frac{\text{The volume at }273^\circ}{\text{The volume at }277^\circ}=1{\cdot}00013$$
$$\therefore\ \frac{181{\cdot}7}{181{\cdot}7-0{\cdot}307m}=1{\cdot}00013$$
$$\therefore\ 0{\cdot}30704m=0{\cdot}0236$$
$$\therefore\ m=<0{\cdot}08$$

That is, only a very small quantity of trihydrol breaks up between 273–277°, and we can regard the point of maximum density as the close of the $(H_2O)_3 \rightarrow (H_2O)_2+H_2O$ action, or the completion of the melting process.

After 277° A. both

$$2(H_2O)_3 \longrightarrow 3(H_2O)_2 \text{ and}$$
$$2(H_2O) \longrightarrow (H_2O)_2$$

are proceeding, and a rough calculation of their relative importance can be made as follows. From 277-373° there is an expansion. Now $2(H_2O)_3 \longrightarrow 3(H_2O)_2$ represents a contraction from $(2\times 2)$ to $3(1{\cdot}231)=0{\cdot}307$; and $2(H_2O) \longrightarrow (H_2O)_2$ an expansion from $(2\times 0{\cdot}462)$ to $1{\cdot}231=0{\cdot}307$.

If both actions proceeded together at the same rate there would be no change in volume, so that the second one, viz., $2H_2O \longrightarrow (H_2O)_2$ must be proceeding more rapidly than the former one.

At 277° the composition of water is practically the same as at 273° A., viz., 40·4 molecules of $(H_2O)_3$, 59·6 molecules of $(H_2O)_2$, and 59·6 molecules of $(H_2O)$.

The 59·6 molecules of $(H_2O)_2$ will not undergo any further change; but between 277-373° A. let $x$ trihydrol molecules pass into $xH_2O+x(H_2O)_2$

$y$ trihydrol molecules pass into $\frac{3y}{2}(H_2O)_2$

$z$ monhydrol molecules pass into $\frac{z}{2}(H_2O)_2$

The net increase in volume due to these actions is

$$-x(2-1·231-0·462)+y(2-1·846)+\frac{z}{2}(0·615-0·462)$$

$$=-0·307x+0·154y+0·153z.$$

The volume at 277° is 181·7 and as the average coefficient of expansion of water is 0·00045 the volume is increased between 277−373° A. by 7·85.

$$\therefore\quad -0·307x+0·154y+0·153z=7·85$$

$$i.e.,\ -2x+y+z=51·3$$

No likely results are obtained by giving any value to $x$, *i.e.*, the action $(H_2O)_3 \rightarrow (H_2O)_2+H_2O$ ends at 277° (under atmospheric pressure); unless it follows the course.

$$2(H_2O)_3 \rightarrow 2(H_2O)_2+2H_2O$$
$$\rightarrow 2(H_2O)_2+(H_2O)_2$$
$$\rightarrow 3(H_2O)_2$$

Suitable values for $y$ and $z$ can be found so that $p$ at 373° will be 2·04. This condition is satisfied when $x=0$, $y=13$, and $z=38·3$. Water at 373° consists, then, of

$(H_2O)_3$ 27·4
$(H_2O)_2$ 98·3
$(H_2O)$ 21·3

These results are summed up in Table IV.

TABLE IV.

| | $(H_2O)_3$ | $(H_2O)_2$ | $(H_2O)$ |
|---|---|---|---|
| Specific heat (273°) | 0·5 | 0·945 | 1·890 |
| Relative volume | 2 | 1·231 | 0·462 |
| | 4·33 | 2·66 | 1 |
| Density | 0·908 | 0·983 | 1·310 |
| *Percentage comp. of water* | | | |
| 273° By weight | 40·4 | 39·7 | 19·9 |
| By number | 25·3 | 37·3 | 37·3 |
| 373° By weight | 27·4 | 65·5 | 7·1 |
| By number | 18·6 | 66·8 | 14·5 |

As the observed specific heats and the degrees of association of water are practically constant, compared with many other liquids, the product of $p$ and $s$ is almost constant between 273-373° A., ranging from 1·89 to 2·06. In finding the "molecular weight" (*i.e.*, the polymericular weight) of a liquid ($x$) at 273° A.,

$$p_x^{273}=\frac{k}{W_x S_x}$$

For water, $p=1·88$

$s=1·0054$

$w=6$

$\therefore\ k=11·34$

$$\therefore\ p_x^{273}=\frac{11·34}{W_x S_x}$$

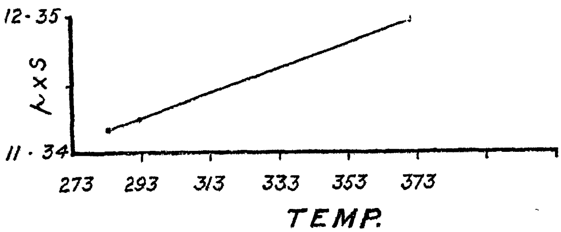
$$\text{and}\ p_x^{373}=\frac{12·36}{W_x S_x}$$

The values of $k$ at other temperatures can be obtained from Table V. or Fig. 1.

TABLE V.

| Absol. Temp. | $p \times s$ (*See* ST, Table III). | R | Absol. Temp. | $p \times s$ | R |
|---|---|---|---|---|---|
| 273° | 1·89 | 11·34 | 323° | 1·99 | 11·94 |
| 283° | 1·92 | 11·52 | 333° | 2·01 | 12·06 |
| 293° | 1·93 | 11·58 | 348° | 2·02 | 12·12 |
| 303° | 1·96 | 11·76 | 363° | 2·04 | 12·24 |
| 313° | 1·97 | 11·82 | 373° | 2·06 | 12·36 |

FIG. I.



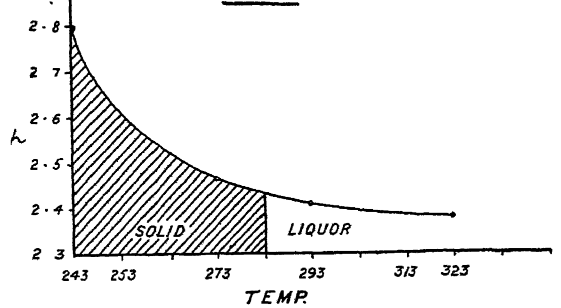

The specific heats of a few liquid inorganic compounds have been determined, and from them their degrees of polymerisation have been calculated. See Table VI.

TABLE VI.

| Compound | Absol. Temp. | Liquid. ST. | $S_{obs.}$ | $p$ | Solid. $p$ | Temp |
|---|---|---|---|---|---|---|
| AgCl ... ... | 767 | 0·191 | 0·129 | 1·48 | 1·48 | 330 |
| AgBr ... ... | 769 | 0·146 | 0·076 | 1·92 | — | — |
| TlCl ... ... | 751 | 0·115 | 0·059 | 1·95 | — | — |
| $PbCl_2$ ... | 811 | 0·148 | 0·121 | 1·22 | 1·59 | 333 |
| $PbBr_2$ ... | 811 | 0·113 | 0·078 | 1·45 | — | — |
| $PbI_2$ ... ... | 646 | 0·0877 | 0·0645 | 1·36 | — | — |
| $LiNO_3$ ... | 549 | 0·958 | 0·390 | 2·45 | — | — |
| $NaNO_3$ * ... | 623 | 0·672 | 0·430 | 1·56 | 2·07 | 329 |
| $KNO_3$ ... | 733 | 0·677 | 0·333 | 2·03 | 2·03 | 329 |
| $AgNO_3$ ... | 518 | 0·385 | 0·187 | 2·06 | 2·00 | 330 |
| $K_2Cr_2O_7$ .. | 713 | 0·509 | 0·335 | 1·52 | 1·92 | 309 |
| $KClO_3$ ... | 550 | 0·538 | 0·325 | 1·66 | 2·01 | 307 |
| $H_2SO_4$ (solid) | 243 | — | — | — | 2·80 | 243 |
| $H_2SO_4$ (solid) | 273 | — | — | — | 2·48 | 273 |
| $H_2SO_4$ (liquid) | 293 | 0·8315 | 0·3447 | 2·41 | — | — |
| $H_2SO_4$ (liquid) | 323 | 0·8524 | 0·3585 | 2·38 | — | — |
| $SO_2$ (solid) ... | 127 | — | — | — | 1·81 | 127 |
| $SO_2$ (liquid) | 253 | 0·516 | 0·313 | 1·65 | — | — |
| $SO_2$ (liquid) | 273 | 0·532 | 0·317 | 1·67 | — | — |
| $Na_2S_2O_3.5H_2O$ | 329 | 1·064 | 0·569 | 1·86 | — | — |
| $Na_2HPO_4.12H_2O$ | 343 | 1·492 | 0·758 | 1·96 | — | — |
| $CaCl_2.6H_2O$ | 340 | 1·159 | 0·552 | 2·10 | — | — |
| $NH_3$ (solid) | 85 | 1·858 | 0·5 | — | 3·72 | 85 |
| $NH_3$ (liquid) | 273 | 2·678 | 0·876 | 3·05 | — | — |

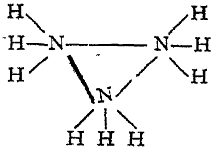
The results in Table VI. are not only interesting but perplexing. We should expect that $p$ would be less in the liquid than in the solid state. Taking ice at 273° as trihydrol, $p$ for AgCl., $KNO_3$, $AgNO_3$, &c., is practically the same at the M.P. in both the liquid and solid states; so is it for $H_2SO_4$ and $SO_2$. The polymerisation curve for $H_2SO_4$, &c., is practically continuous on change of state (see Fig. II.). There is a fall in

FIG. 2.

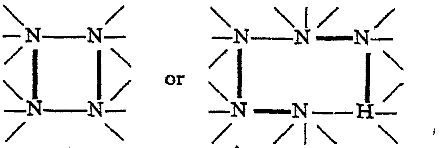



the value of $p$ on melting for $K_2Cr_2O_7$, $KClO_3$, $H_2O$, &c ; but a rise in the cases of P, Bi, Ga, Hg, $LiNO_3$(?), AgBr, &c. To make $p$ always greater in the solid state than in the liquid state we should have to assume that ice at 273° was $(H_2O)_4$, or more complex still, for all the values of $p$ (in the solid state) are based on $(H_2O)_3$ at 273° (ice).

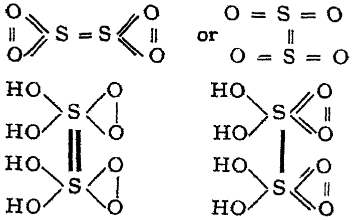
When $p$ is greater in the liquid than in the solid state I should imagine it is for the same reason that $p$ for water is greater at 373° than at 273° A. So, solid phosphorus ($P_1$ and $P_2$) on melting becomes more associated still, *i.e.*, $P_2$, $P_4$, $P_8$, &c. In the liquid state $p$ for $NH_3$ is probably 3, so that N is pentavalent;



in the solid state ammonia also contains either $(NH_3)_4$ or $(NH_3)_6$.



It is possible to give sulphur a very high valency in both liquid $SO_2$ and $H_2SO_4$. Thus :—



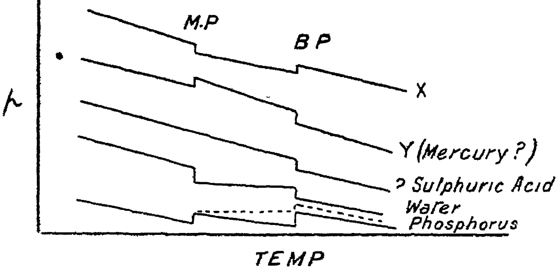
We can divide the polymerisation curves into five classes :—

1. The sulphuric acid curve.
2. The water curve.
3. The P or S curve.
4. X } See Fig. III.
5. Y }

The sulphuric acid curve shows a gradual and continuous fall in the value of $p$ until the boiling point, when $p$ becomes less than 1 (*i.e.*, counting $H_2O$, $SO_3$ as half molecules. $p$ for these separate parts is 1+).

The water curve shows a distinct fall in the value of $p$ at the M.P., and again at the B.P. The P curve shows a rise probably at the B.P. as well as the M.P. X and Y are two theoretical curves.

FIG. 3




(To be continued).

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## OSMOTIC PHENOMENA.*

By CHARLES A. SHULL,
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A THOUGHTFUL consideration of the various relationships which exist between plants and their environment, leads one to the conclusion that none is of gerater importance than the relationship established with the moisture of the soil through the roots and root hair mechanism. The fundamental character of this relation is seen clearly in the facts that soil moisture is the dominant edaphic factor in the geographic distribution of vegetation, and that some of the most striking modifications in the form and structure of plants are produced by physical or physiological dryness of the environment. The deserts of the earth have a sparse vegetation not because of infertility, but from low soil moisture content. And the succulent types of plants found in xerophytic and halophytic habitats have been developed through the physiological conditions set up inside the plant incident to low availability of water.

As has been shown recently by MacDougal and others, the course of carbohydrate metabolism is determined in certain succulents by the amount of water existing in the cells, and the probability is that most succulent plants have been modified by the osmotic conditions in their cells. Whenever the water content exceeds the critical amount, the carbohydrates form polysaccharides of low imbibitional capacity. But if the saturation deficit becomes great enough, the tendency is for the carbohydrates to go over into pentosans which are hydrophilous. In such cases, if in addition there is the production of much free acid during the carbohydrate transformations, succulence will probably result from the combination of circumstances. Thus low availability of soil moisture may fundamentally change the metabolism of the plant, and modify its whole form and structure.

Whether we consider the influence of the plant upon soil moisture, or *vice versa*, the influence of the quantity of soil moisture upon the plant, these influences must act through the same mechanism,

*A Contribution to a General Discussion on "Physico-Chemical Problems Relating to the Soil" held by the Faraday Society, on Tuesday, May 31, 1921.

the osmotically active membranes of the plant. Usually these are living membranes, but osmotic membranes of cellulose, and dead cells, as in seed coats, are now well known.

When dry seeds with osmotically active coats are placed in moist soil, they absorb moisture with great power, such forces an imbibition, capillarity, surface force, hydration power of colloids, and osmotic pressure from internal salts being involved. The total power of the seed to absorb water is the resultant of all these forces working together. Opposed to these internal forces are external forces which tend to prevent intake of water. The surface forces of soils, capillarity, surface tension, adhesion, cohesion of water in thin films, osmotic action of solutes, &c., are pitted against these internal forces; and water movement into or out of the seed will take place in accordance with the lack of equilibrium between the two resultant forces It is an interesting fact that seeds will actually germinate in a soil that has a moisture content below its wilting coefficient.

As soon as the seed begins to germinate, the characteristic osmotic mechanism for soil water intake is established. The view point is general that the intake of water, its transfer through the plant body, and its distribution to the living cells, are processes involving osmotic action at various places in the organism. Although some suggestions have been made assigning to the root a rather passive rôle in water intake, it seems to me a mistake to adopt the idea that the root is mainly an anchorage organ, and that water merely filters through the root under the negative pressure of atmospheric evaporation and the cohesion of water. The osmotic delivery of water by the root to the lower end of the cohesive water columns probably goes on at a rate determined by all of the physical and chemical conditions within the soil-root system, including the cohesive pull upon the root cells. And if this does not keep pace with evaporation, the deficit in the aerial portions becomes greater and greater, and the tension stronger, until breakage of the column and permanent wilting ensues.

There is reason for believing that the drying power of the atmosphere, which fluctuates greatly with changes in relative humidity, averages not far from 1000 atmospheres. And this is the tremendous force which is responsible for the disturbance of moisture equilibrium in the leaves, generating in the cell walls bounding intercellular spaces, in the protoplasm itself, and in the vacuoles of leaf cells, those imbibitional and osmotic forces which lift the water column of the transpiration stream to the tops of even the tallest plants.

The root hair itself is very well adapted to its function as an absorbing organ. As Miss Roberts has shown, the wall of the root hair is usually the outgrowth of the middle lamella of the epidermal cell. It is lined inside by a cellulose layer deposited upon it by the living protoplasm. The external layer, therefore, is largely calcium pectate, and a pectin mucilage brings it into almost intimate contact with the particles of soil minerals. As this pectic material is a hydrophilous colloid, it is highly adapted to imbibe surface moisture from the particles of soil with which it is in contact. It is worth while to note in passing that the whole problem of water intake and water outgo from the plant begins and ends in imbibition, imbibition of water from the protoplasm and vacuole by the exposed cell walls in leaf interspaces, and imbibition of water from the surface of soil particles by the pectic walls of absorbing root hairs.

There are several main problems connected with the osmotic phenomena of plant life which are worthy of consideration. These are, the nature of osmotic pressure itself, the cause of semipermeability in membranes, and the cause of unilateral movement of water across the semipermeable septum. Before considering the nature of osmotic pressure, the power of the plant to adjust itself osmotically to its environment should be mentioned. It has been fully established by the work of Hill, Drabble, and Drabble, and Miss Roberts, that the plant increases or decreases the osmotic concentration of its cell sap *pari passu* with changes in the environment which determine the scarcity or availability of water for the plant. Miss Roberts' work is especially significant as related to soil moisture, since she made her determinations on root-hair producing cells. She found that the osmotic pressure of the root hairs is maintained a few atmospheres in excess of that of the surrounding medium. Such changes in the root cells are accompanied by corresponding changes in the osmotic mechanism more or less throughout the entire plant, so that appropriate osmotic gradients are constantly maintained. With plants growing in the soil, a similar gradient for moisture intake exists. At the wilting coefficient the soil withholds water from the plant with a force of about four atmospheres, while the usual osmotic concentration of the sap of root cells of land plants is seven or eight atmospheres. In desert regions, of course, these pressures would run much higher. Under normal field conditions, therefore, the pressure gradient in ordinary mesophytic plants should run from four to eight atmospheres, as the fluctuation of the water withholding power is from zero to four atmospheres. At the wilting coefficient the effectiveness of the intake gradient is lost because the rate of transfer of moisture from soil particle to soil particle toward the plant becomes entirely inadequate. And now, even though the plant's osmotic pressure rises rapidly, it does not succeed in securing the needed moisture, because it is trying, as it were, to draw water from a dry well. Permanent wilting must quickly ensue in most cases after the soil reaches the wilting coefficient.

The main criticism to be made of the current discussions of the nature of osmotic pressure is that they attempt to simplify too much a process that must, like other life processes, be complex. We may attribute osmotic pressure to the difference in free energy of the solvent and solution, or to the kinetic energy of the solute acting on the semipermeable membrane. It seems to me more appropriate to consider osmotic pressure a complex force, the resultant of numerous factors. The free energy of the solvent, the kinetic energy of the solute, the chemical forces of hydration, especially in more concentrated solutions, and the attraction of ions in solution for particles of water charged oppositely while passing through the differential septum, are all factors in producing osmotic pressure. In the plant this complex force

is smallest in the root hairs, and progressively increases to the farthest limits of water transfer.

The most important problems in connection with osmosis centre in the nature and causes of semipermeability in membranes. The sieve theory, the various solubility theories, the surface tension theory, and the hydrone theory are all well known. Every one of them has some supporting evidence, but all of them have their limitations, and prove inadequate to account for the known facts.

Armstrong's hydrone theory has come particularly to my attention in connection with my own work. The assumptions which are made in this theory as to the character of semipermeable membranes and the salts which they eclude from passage are of such a nature that they seem to me to necessitate the fundamental likeness in behaviour of all semipermeable membranes. If only hydronated membranes can exhibit semipermeability, and if hydronated membranes exclude all hydronated or hydrolated salts, then all membranes of this kind should have identical behaviour. The variability in behaviour of the natural semipermeable membranes, then, is a challenge to the hydrone theory.

Again, it is not possible to attribute semipermeability to some particular chemical substance in the membrane, like tannin, or suberin, or cutin, &c. Many different kinds of membranes are semipermeable, and no single substance, or class of substances, is common to them all. When copper ferrocyanide and other chemical precipitates, cellulose cell walls, or suberised cellulose, gelatin tannate, celloidin, cutinised tissue, parchment paper, and living protoplasm all exhibit semipermeability, it is certain that this peculiar property does not depend on chemical composition, but must be related rather to the structure of the membrane.

There is one property which all of these membranes have in common. They are all colloidal gels. It is my opinion that any theory of semipermeability should frankly recognise this property, and be couched in the language of the physics and chemistry of colloidal matter.

Water can undoubtedly penetrate both phases of the colloidal gel; but salt molecules attempting to penetrate the membrane would probably be prevented from travelling through the disperse phase by surface tension and other surface forces on the contact surfaces between the disperse and continuous phases. If so, they would have to travel in the contiuous phase.

Recently Free has proposed a theory of protoplasmic permeability based upon this conception. He assumes that protoplasm is made up as a two-phase system in which the phases differ mainly in their percentage of water content, arranged as colloidal globules dispersed in a colloidal medium. These two phases are supposed to be so related that interchange of water between the two can occur accordingly as changes in the physics or chemistry of metabolism, or of the environment, necessitate. By such changes, the colloidal globules may increase in size while the continuous phase decreases; or, *vice versa*, the globules may become smaller while the continuous phase separating them increases in thickness at their expense. Conceivably the globules might reach such a size that the continuous phase would remain as the thinnest possible films between them, or they might enlarge until the gel is reversed, the discontinuous phase becoming a continuous medium, and the former continuous phase becoming discontinuous.

Changes in permeability and semipermeability would be related to these phase interchanges Semipermeability would exist when the continuous phase existed in such thin films that molecular diffusion through it was impossible. Adequate provision is found here for natural differences in membranes, for they could hardly have identical behaviour unless the colloidal material were identical in kind. Two different kinds of membranes could exhibit differences in reaction toward the same solution, and one would not expect to find semipermeability behaviour identical in all membranes.

It seems clear to me that we must have a theory of semipermeability that recognises the nature of the membrane as Free's theory does. Living protoplasm is an amphoteric substance with an isoelectric point; and it may react as an acid or base depending on hydrogen ion concentration. As it is played upon by various solutes, or by temperature, or light, changes in the permeability or semipermeability relations would undoubtedly occur according to the nature of the solutes, and the effects of other factors on the aggregation in the colloidal system. In non-living membranes like seed coats, the gels are much firmer, more difficult to change, and the characters more stable than in living protoplasm. But even here one might expect changes from permeability toward semipermeability, or *vice versa*, with reagents having powerful effects on collöidal aggregation. In the problem of soil-moisture intake by roots, of course, we are dealing with a very delicate protoplasmic gel.

Finally, the movement of water through the membrane offers an interesting problem. When the osmotic cell is completely surrounded by the solvent, like an enclosed sack, and if the membrane is elastic, one can think of the pressure moving the membrane outward in every direction to include more water, rather than water moving in through the membrane. It is the membrane that moves. But in the living plant osmotic and imbibition forces set up a unilateral movement which has not been satisfactorily explained. The suggestions of Pfeffer as to protoplasmic differences on opposite sides of the cell, and of differences in concentration on opposite sides of the vacuole are too well known to need discussion. Rhythmic pulsations of the osmotically active cells cannot be assumed.

A suggestion which merits attention has recently been made by Loeb. In amphoteric membranes like the protoplasm of root hairs, and of vacuolate cells generally, the opposite sides of the membrane may be oppositely charged. If they were, Loeb points out that positively charged water particles would be driven through the membrane from positive toward negative side, where it would lose its charge after completing passage. The loss of charge allows other positively charged particles to follow; and if a whole series of cells one after the other had such properties, the series would set up a unilateral current of water; in the case of roots let us assume toward the open tracheæ of the vascular system. At least this is one of the possible factors in addition to osmotic pressure

gradients, and might be responsible in part for the removal of water from the cortical cells into the open tracheæ. Electric exosmose has been suggested to account for the glandular secretion of water from cells of high osmotic concentration into ducts with lower concentrations. It can just as easily be a factor in the secretion of water into the tracheæ of roots.

The plant and its whole environment may be looked upon as a system in which atmospheric evaporation is the chief disturber of moisture equilibrium. In response to this disturbance, imbibitional and osmotic forces are set up which reach back from leaves to roots through cohesive water columns. These water columns are fed from below by an active root system which delivers its water by osmotic action and possibly electric transfer of water. The water is imbibed by the hydrophile colloids of the root hairs, from the surface of contiguous soil particles, which in turn exert surface tension, surface, and capillary forces to draw moisture from particle to particle toward the plant. This disturbance finally reaches to the ground water surface, which slowly lowers as the result of this upward movement of water during periods of no precipitation, but is maintained by precipitation from the same atmosphere which, when dry, disturbs the water equilibrium.

I am fully aware that there are many points which need investigation before an entirely satisfactory picture of the osmotic phenomena of plant life can be drawn. They are very complex phenomena, perhaps much more complex even than the considerations here brought forward indicate. But with a working hypothesis such as I have briefly outlined, we should be able by appropriate investigations to throw much light on those more or less obscure regions of the problem.

## NEW BRITISH CHEMICAL STANDARD STEELS.

(Analytically Standardised Turnings)

Two new plain carbon steels standards are now read for issue, viz., "M", needed for some time mainly for colour carbon tests round about 0·23 per cent, and "0 1" which fills the vacancy for a colour carbon standard of about 0·33 per cent, in addition to being available for the other elements shown below.

The analyses have been undertaken as usual by a number of experienced chemists representing the following interests: British Government Department; U.S. Bureau of Standards; Referee Analysts, independent; Railway Analysts, representing users issuing specifications; Works Analysts, representing makers and users.

The standard figures are as follows:

| | "M. | "01." |
|---|---|---|
| Carbon | 0·228 | 0·333 |
| Silicon | 0·057 | 0·162 |
| Sulphur | 0·05* | 0·032 |
| Phosphorus | 0·04* | 0·031 |
| Manganese | 0·6* | 0·617 |
| Arsenic | — | 0·024 |
| Chromium | — | 0·0170 |
| Copper | — | 0·037 |
| Nickel | — | 0·162 |

* approximate.

The standards may be obtained either direct from Organising Headquarters, 3, Wilson Street, Middlesbrough; or through any of the leading laboratory furnishers at a price just sufficient to cover the cost. A certificate, giving the names of the analysts co-operating, the types of methods used, and a detailed list of their figures, will be supplied with each bottle.

## ILLUSTRATION OF MOLECULAR MOTION.*

By J. NORMAN TAYLOR,
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A proper appreciation by secondary school students of the "habits of Nature," which are expressed in abstract statements called "laws" because of their unfailing truth, is more readily brought about if concrete examples are given to illustrate their application.

For instance, it is very difficult for an immature mind to appreciate the modern theory of the composition of matter. When it is said that matter is not continuous but is of its own nature discrete, *i.e.*, composed of unit particles known as molecules, it is difficult for the student to grasp the full meaning of this abstract statement. His idea regarding the behaviour of these molecules is also a vague one. It is very hard for him to visualise the movements of particles infinitely small, contained in a transparent vessel, and themselves invisible. If he can perform an experiment which will illustrate to him how molecules move very rapidly in straight lines until they collide with each other or come into contact with the walls of the containing vessel, then he will be able to perceive that molecules are elastic. He will also be able to accept the postulate that the interstices between the molecules must of necessity be larger than the molecules themselves. Furthermore, if a student is enabled, through an appropriate illustration, to understand that when heat is applied to the system the molecules move much more rapidly, then he will be in a much better position to take up the study of the gas laws. He will also be enabled to understand more thoroughly the kinetic theory of gases which is based upon all of these considerations.

A device illustrating the assumed behaviour of molecules, and described by E. R. Stoekel in *Science*, xlviii., No. 1245, has been employed by the writer in assisting chemistry students to a better understanding of the molecular theory. It consists essentially of a hard glass tube about 10in. in length and 1in. in diameter, containing a pool of mercury which supports a small quantity of finely crushed material. In using this form of apparatus in the Association School laboratory it has been found that particles of cobalt glass of twenty mesh are very satisfactory. After preparing the tube, as here indicated, it is evacuated so that a pressure of less than a millimeter obtains and is then sealed from the pump. During the subsequent demonstration the tube may be held in the hand without inconvenience, but may, if desired, be clamped to a standard.

Upon the application of heat to the mercury

*Reprinted from June, 1920, issue *School Science and Mathematics* XX, No. 6.

pool and upon gradually increasing the temperature, the particles on the surface "were carried away by the evaporating mercury" and moved about in the upper part of the tube in much the same manner as gas molecules are presumed to behave.

After completion of the demonstration by the instructor each student may be allowed to verify the experiment. The use of this simple device excellently enables the student to form a clear mental picture of how the very small gas molecules are supposed to be in constant motion, and how the speed of this motion is altered by changes in temperature.

## NEW PROCESS FOR THE MANUFACTURE OF SODIUM PERBORATE.

The New York *Journal of Commerce* of April 21 contains an article on an invention which has just been patented by the Norwegian firm Fredrikstad Elektrokemiske Fabriker, for producing sodium perborate, a bleaching powder which has been known and used since the beginning of the 20th century, but which has never been produced in Norway or in Sweden.

The process consists of an electrolysis of common borax in a weak solution. In this way the borax combines with a large percentage of oxygen. One of the disadvantages inherent in the processes utilised hitherto has been that a large percentage of electric energy and borax were wasted. Another disadvantage was that only chemically pure borax could be used, and finally, a third disadvantage consisted in the difficulty of maintaining a continuous and constant production.

Both of these last-named disadvantages have been overcome by adding to the original borax solution a certain amount of sodium cyanide. This addition makes all the impurities harmless, and prevents decomposition of the perborate, which is formed in the solution. Accordingly, it is possible to utilise raw material less pure, and therefore less expensive, thus lowering the cost of production. Continuous production is also made possible.

When the solution is saturated it is poured out and cooled; thereupon a certain amount of sodium superoxide is added which causes a rapid crystallisation of the perborate.

This new bleaching powder has many properties which make it suitable for a number of practical purposes. It is, for instance, a very good antiseptic, and may be used in the treatment of cuts, wounds, &c., both as a powder and dissolved in cold water. It is particularly good as a bleaching agent in the textile industry, and in washing clothes. As a bleaching agent it is absolutely harmless. It may also be used for starching clothes.

## FORTHCOMING FAIRS.

Royal Agricultural Show, Derby. June 28-July 3. Includes agricultural machinery and forestry.

London Fair and Market. Royal Agricultural Hall, Islington, July 4-15. Apply to International Trade Exhibitions, Ltd., Broad Street House, New Broad Street, London, E.C.2.

Confectioners' and Bakers' Exhibition. Royal Agricultural Hall, Islington, September 3-9. Apply to 31, Queen Victoria Street, London, E.C.4.

Shipping, Engineering, and Machinery Exhibition. Olympia, September 7-28. Apply to Mr. F. W. Bridges, Exhibition Offices, 36-38, Whitefriars Street, London E.C.4.

Grocers' Exhibition. Royal Agricultural Hall, Islington, September 17-23. Apply to 31, Queen Victoria Street, London, E.C.4.

11th London Medical Exhibition. Central Hall, Westminster, S.W.1, October 3-7. Apply to *British and Colonial Pharmacist*, 194-200, Bishopsgate, London, E.C.2.

International Shoe and Leather Fair. Royal Agricultural Hall, October 3-7. Apply to Manager, *Shoe and Leather Record*, 40, Finsbury Square, London, E.C.2.

Fifth International Commercial Motor Exhibition. Olympia, London, October 14-22. Apply to Exhibition Manager, Society of Motor Manufacturers and Traders, Ltd., 83, Pall Mall, London, S.W.1.

15th International Motor Exhibition. Olympia, and White City, London, November 4-12. Apply to Exhibition Manger, Society of Motor Manufacturers and Traders, Ltd., 83, Pall Mall, London, S.W.1.

7th Cycle and Motor-Cycle Show. Olympia, London, November 28-December 3, 1921 Apply to General Manager, British Cycle and Motor-Cycle Manufactures' and Traders' Union, Ltd , The Towers, Warwick Road, Coventry.

Lemberg, Poland. An Industrial and Agricultural Fair is being arranged in Lemberg, Poland, in September, by the Targi Wschodnie (Eastern Fairs & Markets, Ltd.), of Lemberg, a society organised to promote trade throughout Poland and South Russia. They would like to correspond with any companies interested in East European trade. Exact dates of Fair will be announced later.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

*Ordinary Meeting, June 9, 1921.*

Prof. C. S. Sherrington, President, in the Chair.

The following papers were read :—

*"Break-shock Reflexes and 'Supramaximal' Contraction-response of Mammalian Nerve-muscle to Single-shock Stimuli."* By Prof. C. S. Sherrington.

The maximal twitch-contraction of tibialis anticus muscle (cat) evoked by a single break-shock applied to the cut motor nerve is compared with the same muscle's contraction as evoked reflexly (spinal preparation) by a single break-shock applied to an afferent nerve. The reflex contraction is found to exceed the former when the break-shock for the former is even considerably weaker than that employed for the latter. Evidence is given that this is due to the reflex response being tetanic in nature. If the break-shock is, however, quite strong (*i.e.*, above the limiting maximal value of Forbes and Gregg) there is evidence

that it excites, even when applied to the motor nerve, a response of tetanic quality. The so-called "over-maximal twitch" is in reality a response of this kind. Such responses are in this paper termed "supra-maximal responses."

Probablitiy is shown that a reaction of like kind obtains in the afferent nerve when the single-shock applied to it is of comparably high value. In this latter case there is added to the tetanic reaction of the spinal centre a tetanic reaction from afferent nerve-fibres themselves. But with weak and moderate break-shock stimuli the seat of origination of the tetanic character of the reflex discharge appears to lie mainly, if not wholly, in the centre itself. It is inferred that it arises there from a process, a "charge" process which is relatively long-lasting in comparison with the cycle of a nerve-impulse, a process which is more intense and of longer duration when the afferent fibres excited are many than when they are fewer.

*"Dictyokinesis in Germ Cells, or the Distribution of the Golgi Apparatus during Cell Division."* By R. J. LUDFORD and J. B GATENBY.

Matuiation mitoses in the germ-cells of Cavia, Mus, Helix, Limnæa, and Stenobothrus were examined in order to ascertain the fate of the Golgi apparatus during cell-division.

In all cases the Golgi apparatus is found to separate or break up into its constituent granules or rods, and these are distributed haphazardly to the two daughter-cells at mitosis.

The Golgi apparatus is, in no case examined, divided out between the daughter-cells as carefully and equally as are the chromosomes. This appears to show that from the point of view of a mathematical conception of the hereditary processes, the Golgi apparatus does not share to any important extent, if at all, in the transmission of factors from cell to cell.

*"The Effect of Red Fatigue on the White Equation."* By F. W. EDRIDGE-GREEN, M.D.

A white equation is formed by means of a mixture of a red of $\lambda 6670-6770$ A°, a green of $\lambda 5144-5156$ A°, and a violet of $\lambda 4250-4267$ A°, matching a simple white.

When the eye is fatigued with light viewed through a red glass which transmits from $\lambda 630\mu\mu$ to the end of the red end of the spectrum, or with pure spectral light in the region of $\lambda 670\mu\mu$, and the equation is again made, the amount of green is about half that required for the equation made with the unfatigued eye.

The white equation and its match cannot be due to similar physiological processes, or both would change in the same ratio.

When the fatiguing light is in the region of $\lambda 780\mu\mu$, no difference is seen between the mixed and simple white.

*"A Method for Investigating the Hæmolytic Activity of Chemical Substances."* By E. PONDER.

1. A technique for the investigation of the hæmolytic action of chemical substances is described.

2. The relation between the time taken by a given quantity of hæmolytic substance and the temperature at which it acts is expressed by a hyperbola.

3. Equations are given expressing the relation between the constants of such a hyperbola and the quantity of hæmolytic substance to which the hyperbola applies.

4. Certain general relations which have been found to hold for all substances examined in connection with this research are pointed out.

5. A comparison between experimental and calculated results is given.

*"The Development of Vegetation in the English Lakes, considered in Relation to the General Evolution of Glacial Lakes and Rock Basins."* By W. H. PEARSALL.

The data presented show that a very close connection exists between the flora (and fishes) of the English Lakes and the physical and chemical conditions of their shores and waters. These lakes are of the same age (glacial), of similar origin, and lie among rocks possessing relatively uniform characters. It is therefore possible to attribute the differences they show to variations in the rates or errosion and sedimentation of the lake basins, due to inequalities in the durability of the underlying rocks In distinguishing *rocky* from relatively *silted* lakes, a contrast is therefore made between *primitive* and more highly *evolved* lakes, and it becomes possible to describe the stages in the post-glacial development of a rock basin. The conception has particular value biologically, since it permits the study of the post-glacial development of vegetation. The two extreme phases here distinguished differ in the following particulars :—

| | Primitive. | Evolved. |
|---|---|---|
| Per cent of drainage system cultivable ... ... | 5–8 | 17–45 |
| Per cent of lake shore rocky (to 9 *m.*) ... .. | 73–47 | 27–12 |
| Per cent of *Isoetes* and *Nitella* ... ... ... ... | 85–74 | 52–30 |
| Per cent of *Juncus fluitans* | 8–5 | 2–0 |
| Per cent of *Potamogeton Naias* ... .. ... .. | ½–2 | 30–55 |
| Phyto-plankton ... ... | Desmids dominant | Diatoms dominant |
| Fish .. .. .. ... ... | Chiefly trout. | Chiefly perch and pike. |

Evidence is adduced for considering all these differences as ultimately dependent upon the physical condition of the lakes.

## CHEMICAL NOTICES FROM FOREIGN SOURCES

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. clxxii., No. 21.

"Acrylic Acid and Acrylic Ethers. Halogen Derivatives of the propionic Acids and Ethers."—MM. Charles Moureu Marcel Murat, and Louis Tampier.

"Artificial Colouration of Crystals obtained by the Solidification of a Molten Substance, and on Crystalline Diffusion."—M. Paul Gaubert.

"Contribution to the Study of the Oils obtained from Grape Pips."—M. Emile André.

"Application of the Law of Mass Action on the Results obtained in the Reaction of $\beta$-galactosidase on Galactose in Propylic Alcohol Solution."

No. 22.

"Double Catalysis of Vanadic Acid and Oxygenated Water."—M. V. Auger.

"On Furfural Camphor and some of its Derivatives."—Mdlle. Wolff.

"Action of Ethylmagnesium Bromide on Dibenzylidene-cyclohexanone and γ-Methyl-cyclohexanone."—M. Manolesco.

"Influence of Ammonium Molybdate on the Rotatory Power of Certain Sugars."—M. Georges Tanret.

## NOTES.

Faraday Society.—A General Discussion on "Catalysis with Special Reference to Newer Theories of Chemical Action" will take place on September 28 next. During the afternoon session "Radiation Theory" will be discussed, and the opening paper will be given by Prof. J. Perrin (Paris). The evening session will deal with "Heterogeneous Reactions," and it will be opened by Dr. Irving Langmuir (Schenectady, U.S.A.).

The "Sanitas" Company, Ltd.—The General Meeting of the "Sanitas" Company, Ltd., was held at the Cannon Street Hotel, London, E.C.4, on the 15th inst., under the presidency of the Chairman, Mr. C. T. Kingzett, F.I.C., F.C.S., this being the 43rd Annual Meeting held since the incorporation of the original company. The Chairman said it was a matter for congratulation that, notwithstanding the general slump in trade experienced during the year under review, particularly in the export department, and the necessity of writing down stocks acquired at war and boom time high values to current prices, the trade done in the past year had on the whole been satisfactory, sufficing for the payment of the full dividend of 9 per cent on the Preference shares of the Company, and 5 per cent on the Ordinary shares. In view of the great increase in business experienced in the previous year, the Company had acquired and equipped a model factory at Hayes, and were prepared to make use of it as soon as the revival of trade justified the action. "Sanitas Fluid" still held the position of first favourite as the non-poisonous disinfectant and oxidant, devoid of all objectionable qualities, and the sales of that particular article showed a great stride in the year under review. He was also pleased to note improvement in the qualities of the floor polishes, embrocation, and other numerous products of the Company. Their association with Lever Brothers, Ltd., was of the happiest character, and he looked forward to the continued prosperity of the Company's business with full confidence in the competent hands of the Managing Director (Mr. N. F. Kingzett) and his colleagues. The retiring Directors and Auditors were duly re-elected.

Decomposition of Chloracetic Acids.—M. Sanderens has demonstrated by catalysis that organic acids give rise to a cetone with disengagement of carbonic gas. He examined decomposition of the halogen acids, for example $CH_2.Cl.COOH_3$, to ascertain whether symmetric dichloracetone is produced by the action of three different catalysers, thorine, kaolin, and bone-black. With monochloracetic acid, thorine gives a mixture of HCl, $CO_2$, and CO, with a carbon deposit. Decomposition occurs following the same processes with the other two agents, but in the case of trihalogen acid, whereas thorine and kaolin decompose it into complex products, bone-black transforms it into chloroform with a yield of 85 per cent, the remainder being a mixture of $C_2Cl_4$ and $C_2Cl_6$, with a little dissolved hydrochloric acid.—*La Nature*, March 19, 1921.

## New Patents.

This List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

15078—Evershed, H. R.—Process for manufacture of sulphate o lead. May 31.

14986—Farbwerk vorm, Meister Lucius & Bruning.—Manufacture of methylsulphites of secondary aromatic-aliphatic amines. May 30.

15441—Peufaillit, P.—Process for industrially preparing derivatives of bornyl for preparing synthetic camphor. June 3.

15023—Wright, Sir J R.—Production of ammonium salts and coloured pigments. May 31.

*Specifications published this Week.*

163877—Phillips, F. J.—Manufacture of readily soluble alkali silicates.

144659—Badische Anilin & Soda Fabric —Process for transforming ammonia into a salt for use as a fertilizer.

*Abstract Published this Week.*

*Recovering Tin from Scrap.*—Mr. P. Mackay of 70, Lombard Street, London has obtained a Patent No. 161654 for an improved process of recovering tin from Scrap by treating it with oleum to dissolve the tin, the material is then lifted out of the acid and washed in water. Fresh acid is added to replace that used, and another batch is treated. After a time a basic sulphate $Sn\,SO_4$ $Sn\,SO_2$ deposits and is drawn off. The washing water contains some insoluble oxide, $SnO_2$, and some tin in solution. The dissolved tin is recovered by precipitation as sulphide or iron is added to neutralize the acid and obtain metallic tin. External heat is not required in the process, but the acid bath is maintained by by the exothermic heat and the periodical additions of fresh acid at a fairly constant temperature of 44-55° C. and a strength of about 10 per cent. free sulphur trioxide.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

## NEW COMPANIES.

The under-mentioned particulars of New Companies recently registered are taken from the Daily Register compiled by Jordan & Sons, Limited, Company Registration Agents, Chancery Lane, W.C.2.

*Public Company.*

Swanwick Institute & Club, Limited.—(175051)—Registered 4th June, 1921. The Institute, Pentrich Road, Swanwick. To erect and maintain a Social Club and Institute. Nominal Capital: £2,000 in 4,000 Shares of 10/- each. Minimum Subscription: One-fifth part of the total number of shares offered for subscription. Directors: J. Hiel, Wood Dene, Swanwick, G. Elliott (Junior), Hill Crest, Swanwick; G Harwood, High Street, Swanwick, J. Hopkinson, Church Street, Swanwick; A. Walters, Church Street, Swanwick; R. Marsh (Senior), Derby Road, Swanwick; H. Thompson, Derby Road, Swanwick. Qualification of Directors: £5.

*Private Companies:*

Charles Adams & Son, Limited.—(175044)—Registered 4th June, 1921. 1c, Queen Square, Bristol. To carry on the business of Corn and Flour Merchants, Millers, etc. Nominal Capital: £100,000 in 10,000 Shares of £10 each. Directors: C. Adams, 11, Apsley Road, Clifton, Bristol; H. C. Adams, Spring Bank, Stonehouse, Gloucestershire; H. Fleetwood, 13, Alexandra Road, Clifton, Bristol. Qualification of Directors: 1 Share. Remuneration of Directors: To be voted by Company in General Meeting.

Horley's, Limited.—(175047)—Registered 4th June, 1921. To carry on the business of Capitalists, Financiers, Merchants, etc. Nominal Capital: £20,000 in 20,000 Shares of £1 each. Directors: To be appointed by Subscribers. Qualification of Directors: £100. Remuneration of Directors: To be voted by Company in General Meeting. Subscribers: W. Oliver, Madingley, Richmond Bridge, East Twickenham; A. W. Butler, 12a, York Mansions, Battersea Park, S.W.

BRIERLEY & KERSHAW, LIMITED.—(175042)—Registered 4th June, 1921. To acquire and carry on the business of Makers of Flat and Spiral Springs, now carried on at "Roach Spring and Temple Works", Morton Street, Rochdale Nominal Capital £20,000 in 20,000 Shares of £1 each. Directors W. H. Brierley, 83, Southbank Road, Southport. (Governing Director). Qualification of Directors: 1,000 Shares. Remuneration of Directors To be voted by Company in General Meeting

FRANKLIN & RYAN, LIMITED —(175033)—Registered 3rd June, 1921. 50, Cross Street, Erith, Kent To carry on the business of Omnibus, Char-a-banc and Cab Proprietors and Haulage Contractors Nominal Capital £15,000 in 15,000 Shares of £1 each. Directors: J. G Franklin, 50, Cross Street, Erith, Kent, C Ryan, Herbert House, Oaklands Road, Bexley Heath; T. N. Cannon, Mount Eagle, Bexley Heath Qualification of Directors 250 Shares Remuneration of Directors: To be voted by Company in General Meeting.

WRENCH, LIMITED —(175098)—Registered 7th June, 1921. To acquire and carry on the business of Wholesale, Retail, Manufacturing and Dispensing Chemists and Druggists. Nominal Capital £1,000 in 500 Preference Shares and 500 Ordinary Shares of £1 each. Directors: C. H Osmond. Qualification of Directors: £100 Remuneration of Directors: To be voted by Company Subscribers. F. W. Wrench, 12a, Carlton Road, Bournemouth, Robina S Osmond, 15, Florence Road, Boscombe.

KEMCO, LIMITED.—(175134)—Registered 9th June, 1921. 36, Trinity Street, Huddersfield. To carry on the business of Pharmacy and Drug Store Proprietors. Nominal Capital £1,000 in 1,000 Shares of £1 each Directors. H. Dean, Parkston Grove, Honley, Huddersfield; S. Kenworthy, 157, Trinity Street, Huddersfield. Qualification of Directors: 1 Share

W WINDLE & Co., LIMITED.—(175146)—Registered 9th June, 1921. 452, Edgware Road, W.2. To carry on the business of Chemists and Druggists Nominal Capital £500 in 500 Shares of £1 each. Directors: To be appointed by Subscribers Qualification of Directors. 1 Share Remuneration of Directors: To be voted by Company in General Meeting. Subscribers. G W. Knight, 452, Edgware Road, W 2.; Mabel R. Knight, 452, Edgware Road, W.2.

## WETCARBONIZING, LIMITED.
(In Liquidation).

THE Liquidator offers for immediate sale the undermentioned material. All enquiries to H W. Wadsworth, Esq., Ironhurst Peat Factory Ruthwell, Dumfriesshire Terms: Cash with order. Apparatus post free

Thermometers in wooden cases. 0-110°C., 0-220°C., 0-50°C. 2/6 each.

1 Mercury Reservoir, 500 ccs, 2s. 1-8c. No 1 Blow pipe with taps, petrol gas, 15s. Two packets Filter Papers, 11cm. No. 50, 5/- the lot.

1 Set Analytical Weights with Certificate, 0 001 to 50 grams (gold fractions) £3 the set

1 Pipette 50 cc. bulb, 1/- Two Tubulated Bottles, 10 litres each, £2 lot.

6 only W.M. stoppered bottles, 300 ccs. and 1-350 ccs. 9/- the lot.

1 150-volt 1 K.W. Immersion Heater with one plate only, 30/- lot.

Three G.M. Sieves, 200, 150 and 120 mesh respectively, £5 the lot

1 Box (25) Soxhlet Extraction Thimbles, 25 by 100 mm., 10/- lot

4 Resistance Nets, 50 ohms, 2/6 lot. One Liebig's Condenser, No 2228, 2/6.

Two Flex. Metallic Tubes, each 6ft. long, 2/6 lot. 7 W.M. Flat stoppered Bottles, 300 ccs. 7/6 lot. 14 Specimen Tubes, 6in by ⅝in. corked, 2/- lot. Distillation Flasks, with side Tubes—5 off 50 ccs., 2 off 100 ccs. and 5-250 ccs. Squat Spout Beakers—10 off 50 ccs., 1-100 ccs. and 3-300 ccs. and 1 500 ccs, 3/- lot. 12ft ¼in. bore I.R Tubing and 4½ft. 3/16in. bore pressure tubing, 5/- lot.

One set Fractional Weights 0·5 grms. to 0 01 grms., 15/- lot. 53 Test Tubes, 6in. by ⅝in., 7/6 lot.

The Liquidator also offers about 300 Bottles, Jars, Boxes, etc., containing Chemicals, Organic, Inorganic, Reagents, Indicators, etc., being the complete stock of a research laboratory. A list will be sent on application. Lump sum price wanted for the lot. This price to include bottles, etc., containing the material. Buyer must either make himself responsible for packing and despatching or the offer must be substantial enough to permit of the Liquidator employing a skilled Chemist for packing and despatching.

THE owners of British Patent No. 155,627 "EXPLOSIVES" desire to dispose of the Patent or to enter into working arrangements under licence with a firm likely to be interested.

A copy of the specification and full particulars may be obtained from

HERTFORD RECORD CO., Ltd., of LINDSEY HOUSE, 59, LINCOLN'S INN FIELDS, LONDON, W.C.2.

GOVERNMENT New Hessian Sand Bags size 33 by 14 inches, packed 2,000 in Bale, 1d. each delivered. Send 5d. postage for sample Please mention this paper. P. HARRIS, 55, Old Compton Street, London, W.

# NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemical Apparatus, &c, for review or notice to be addressed to the EDITOR.

**SUBSCRIPTIONS**, £1 12s. per annum, payable in advance, should be addressed to the MANAGER.

**BACK NUMBERS and VOLUMES** can be purchased on application to he MANAGER.

THE CHEMICAL NEWS,
97, SHOE LANE, LONDON, E.C 4

## ADVERTISEMENTS.

**All communications for this Department should be addressed to—**

T. G. SCOTT & SON,
63, LUDGATE HILL, LONDON, E C.4.

## UNIVERSITY OF GLASGOW.

APPLICATIONS are invited for a Lectureship in Organic Chemistry; salary £400 to £450 according to qualifications. Applications, stating teaching and research experience and giving the names of three references, to be sent as soon as possible to Prof T. S. PATTERSON. Any available copies of testimonials may also be sent.

## CITY OF BIRMINGHAM EDUCATION COMMITTEE.

HANDSWORTH TECHNICAL SCHOOL.

REQUIRED in September next, the full-time services of a Lecturer, chief subject Metallurgy. The commencing salary offered will depend upon the previous training and experience of candidate. For full particulars apply to the Principal, Handsworth Technical School, Goldshill Road, Handsworth, Birmingham.

## STAFFORDSHIRE EDUCATION COMMITTEE.

APPLICATIONS are invited for the post of PRINCIPAL and HEAD of the METALLURGICAL DEPARTMENT of the COUNTY TECHNICAL COLLEGE, WEDNESBURY, (in succession to Mr. Walter Macfarlane, F.I.C.), at a salary of £600. The person appointed must be a competent metallurgist with good academic qualifications; practical experience in works is essential.

Further particulars and forms of application, which must be returned before 8th July, may be obtained from the undersigned.

GRAHAM BALFOUR,
Director of Education.

County Education Offices,
Stafford.
June, 1921.

## UNIVERSITY OF ABERDEEN.

LECTURER IN CHEMISTRY.

APPLICATIONS are invited for the post of Lecturer in Chemistry. Salary £425 per annum. Candidates should have special attainments in Organic Chemistry.

Applications, together with a full statement of qualifications and the names of two references, should be sent not later than TUESDAY 5th JULY, to the undersigned, from whom further particulars may be obtained.

H J. BUTCHART,
Secretary of the University

FINE private scientific Laboratory for sale owner going abroad. Also contents and possession of residence if desired.—Box 837, c/o T. G. SCOTT & SON 63, Ludgate Hill, London, E C.4.

# INDEX.

END OF VOLUME CXXII.

THE

# CHEMICAL NEWS

AND

JOURNAL OF INDUSTRIAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

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IN THEIR APPLICATION TO

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EDITED BY

*JAMES H. GARDINER, F.Inst.P., F.C.S.*

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# THE CHEMICAL NEWS.

VOLUME CXXIII.

EDITED BY JAMES H. GARDINER, F.C.S.

No. 3194.—JULY 1, 1921.

## POLYMERISATION AMONGST LIQUIDS.

By WILLIAM R. FIELDING, M.A., M Sc, Vict.
Senior Science Master at King Edward VII School, Lytham.

(Concluded from vol. cxxii, p. 293.)

BELOW I have calculated $p$ for a number of typical organic compounds. The results for some hydrocarbons are given in Table VII.

TABLE VII.

| Compound | Absolute Temp. | $S_T$. | $S_{obs}$ | $p$ |
|---|---|---|---|---|
| $C_5H_{12}$ ... ... ... | 273 | 2·682 | 0·512 | 5·23 |
| $C_6H_{14}$ ... ... ... | 298 | 2·713 | 0·527 | 5·15 |
| $C_7H_{16}$ ... ... ... | 298 | 2·683 | 0·504 | 5·32 |
| $C_8H_{18}$ ... ... ... | 298 | 2·661 | 0·505 | 5·27 |
| $C_8H_{18}$ ... ... ... | 345 | 2·767 | 0·578 | 4·79 |
| $C_9H_{20}$ ... ... ... | 298 | 2·638 | 0·503 | 5·24 |
| $C_{10}H_{22}$ ... ... ... | 298 | 2·631 | 0·498 | 5·28 |
| $C_{10}H_{22}$ ... ... ... | 360 | 2·756 | 0·590 | 4·67 |
| $C_{11}H_{24}$ ... ... ... | 298 | 2·618 | 0·501 | 5·22 |
| $C_{12}H_{26}$ ... ... ... | 298 | 2·609 | 0·500 | 5·22 |
| $C_{13}H_{28}$ ... ... ... | 298 | 2·601 | 0·499 | 5·21 |
| $C_{14}H_{30}$ ... ... ... | 298 | 2·590 | 0·497 | 5·21 |
| $C_{15}H_{32}$ ... ... ... | 298 | 2·586 | 0·497 | 5·20 |
| $C_{16}H_{31}$ ... ... ... | 298 | 2·579 | 0·496 | 5·20 |
| $C_5H_{10}$ ... ... ... | 403 | 2·688 | 1·060 | 2·53 |
| $C_5H_{10}$ ... ... ... | 443 | 2·732 | 1·500 | 1·82 |
| $C_6H_6$ (solid) ... ... | 223 | — | — | 5·40 |
| $C_6H_6$ (solid) ... ... | 263 | — | — | 3·82 |
| $C_6H_6$ (solid) ... ... | 273 | — | — | 3·14<br>3·64 |
| $C_6H_6$ (liquid) ... | 283 | 1·7688 | 0·4066 | 4·35 |
| $C_6H_6$ (liquid) ... | 293 | 1·791 | 0·423 | 4·23 |
| $C_6H_6$ (liquid) ... | 313 | 1·819 | 0·4233 | 4·29 |
| | 323 | 1·838 | 0·4502 | 4·09 |
| | 367 | 1·895 | 0·481 | 3·94 |
| $C_6H_{12}$ ... ... ... | 298 | 2·497 | 0·506 | 4·93 |
| $C_6H_5CH_3$ ... ... | 181 | | | |
| $C_6H_5CH_3$ ... ... | 248 | 1·786 | 0·380 | 4·69 |
| $C_6H_5CH_3$ ... ... | 293 | 1·897 | 0·412 | 4·60 |
| $C_6H_5CH_3$ ... ... | 358 | 2— | 0·534 | 3·74 |
| $C_{10}H_8$ (solid) ... | 223 | — | — | 5·3 |
| $C_{10}H_8$ (solid) ... | 288 | — | — | 4·2 |
| $C_{10}H_8$ (solid) ... | 318 | — | — | 4·2 |
| $C_{10}H_8$ (solid) ... | 338 | — | — | 4·1 |
| $C_{10}H_8$ (liquid) ... | 356 | 1·723 | 0·396 | 4·3 |
| $C_{10}H_8$ (liquid) ... | 368 | 1·733 | 0·427 | 4·0 |

*Conclusions.*

1. The paraffins (saturated hydrocarbons) are highly but almost equally polymerised near their boiling-points

2. The unsaturated hydrocarbon, amylene, is much less polymerised than the corresponding paraffin, although it has two free bonds, which would, one would have thought, have given it additional associative power. Compare $C_5H_{10}$ and $C_5H_{12}$

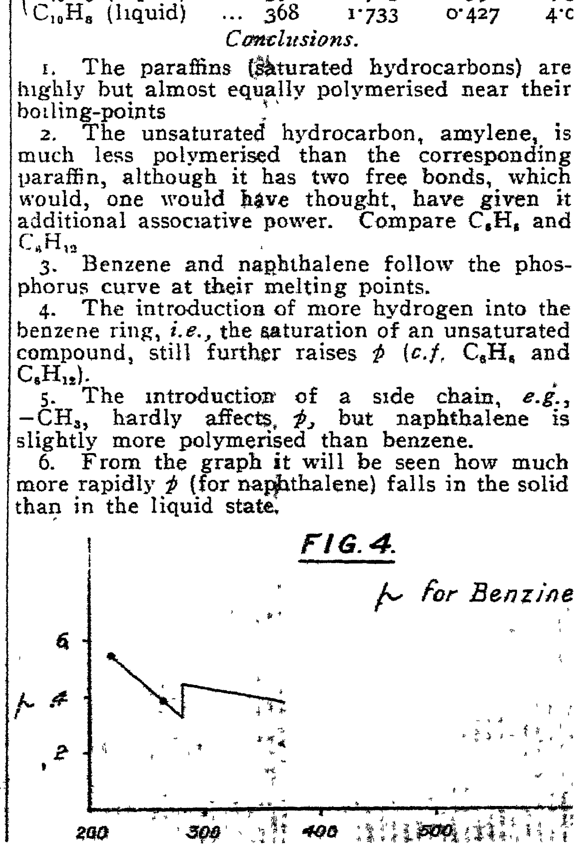
3. Benzene and naphthalene follow the phosphorus curve at their melting points.

4. The introduction of more hydrogen into the benzene ring, *i.e.*, the saturation of an unsaturated compound, still further raises $p$ (*c.f.* $C_6H_6$ and $C_6H_{12}$).

5. The introduction of a side chain, *e.g.*, $-CH_3$, hardly affects $p$, but naphthalene is slightly more polymerised than benzene.

6. From the graph it will be seen how much more rapidly $p$ (for naphthalene) falls in the solid than in the liquid state.

*FIG. 4.*



The influence of the halogens is shown in Table VIII.

TABLE VIII.

| | Compound | T | ST | $S_{obs}$ | $p$ |
|---|---|---|---|---|---|
| $CH_4$ | $CHCl_3$ | 243 | 0·4557 | 0·2293 | 1·99 |
| | $CHCl_3$ | 273 | 0·4730 | 0·2323 | 2·03 |
| | $CHCl_3$ | 333 | 0·5035 | 0·2384 | 2·11 |
| | $CCl_4$ | 273 | 0·3683 | 0·2010 | 1·83 |
| | $CCl_4$ | 343 | 0·3939 | 0·2031 | 1·94 |
| $C_2H_6$ | $C_2H_5.Cl$ | 262 | 1·395 | 0·4276 | 3·26 |
| | $C_2H_5Br$ | 168 | — | 0·195 | — |
| | $C_2H_5Br$ | 244 | 0·808 | 0·205 | 3·94 |
| | $C_2H_5Br$ | 281 | 0·8434 | 0·2164 | 3·90 |
| | $C_2H_5I$ | 243 | 0·5606 | 0·1567 | 3·58 |
| | $C_2H_5I$ | 273 | 0·5825 | 0·1616 | 3·60 |
| | $C_2H_5I$ | 303 | 0·6031 | 0·1666 | 3·62 |
| | $C_2H_5I$ | 333 | 0·6173 | 0·1715 | 3·60 |
| | $C_2H_4Cl_2$ | 273 | 0·9168 | 0·2922 | 3·14 |
| | $C_2H_4Cl_2$ | 303 | 0·9833 | 0·3054 | 3·22 |
| | $C_2H_4Cl_2$ | 333 | 0·9711 | 0·3186 | 3·05 |
| | $C_2H_4Br_2$ | 293 | 0·495 | 0·174 | 2·84 |
| $C_2H_4$ | $C_2Cl_4$ | 243 | 0·394 | 0·1925 | 2·04 |
| | $C_2Cl_4$ | 273 | 0·410 | 0·198 | 2·07 |
| | $C_2Cl_4$ | 373 | 0·445 | 0·228 | 1·95 |
| | $C_2Cl_4$ | 413 | 0·454 | 0·243 | 1·87 |
| $C_6H_6$ | $C_6H_5Cl$ | 308 | 1·2585 | 0·3252 | 3·87 |

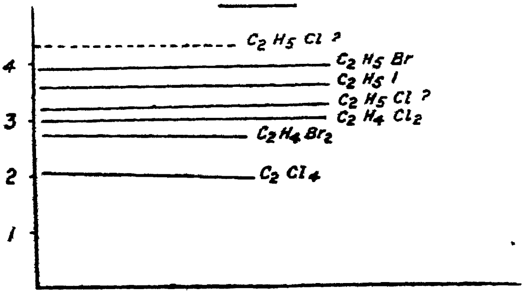
*Conclusions.*

1. The introduction of a halogen either into a saturated, unsaturated, or ring compound has the effect of reducing $p$, and the more complete the substitution of hydrogen the lower does $p$ become (compare $C_6H_6$ and $C_6H_5Cl$; $C_2H_5Br$ and $C_2H_4Br_2$).

2. In some cases there is a rise in the value of $p$ with temperature, *e.g.*, $CHCl_3$ and $CCl_4$ (compare $H_2O$).

3. The polymerisation curves for $C_2H_5I$, $C_2H_5Br$, and $C_2H_4Cl_2$ are practically horizontal. It almost looks as if the specific heat of $C_2H_5Cl$ was inaccurate, as the polymerisation curve for this compound should be above, and not below, that of the corresponding bromine compound. Compare the results for $C_2H_4Cl_2$ and $C_2H_4Br_2$. See Fig 5.

FIG 5.




TEMP

The results for the alcohols are given in Table IX.

TABLE IX.

| | T | ST | $S_{obs}$ | $p$ |
|---|---|---|---|---|
| HOH | 273 | — | — | 1·88 |
| $CH_3.OH$ | 280 | 2·1515 | 0·5901 | 3·64 |
| $CH_3.OH$ | 306 | 2·215 | 0·645 | 3·43 |
| $C_2H_5.OH$ | 182 | — | 0·457 | — |
| $C_2H_5.OH$ | 253 | 2·154 | 0·5053 | 4·26 |
| $C_2H_5.OH$ | 313 | 2·342 | 0·6479 | 3·61 |
| $C_2H_5.OH$ | 353 | 2·384 | 0·7694 | 3·09 |
| $C_3H_7OH$ | 269 | 2·256 | 0·5186 | 4·35 |
| $C_3H_7OH$ | 293 | 2·328 | 0·579 | 4·02 |
| *n* $C_4H_9OH$ | 340 | 2·456 | 0·689 | 3·56 |
| *iso* $C_4H_9OH$ | 206 | — | 0·508 | — |
| *iso* $C_4H_9OH$ | 283 | 2·347 | 0·5022 | 4·67 |
| *iso* $C_4H_9OH$ | 313 | 2·392 | 0·6482 | 3·69 |
| *iso* $C_4H_9OH$ | 358 | 2·481 | 0·8413 | 2·95 |
| amyl $C_5H_{11}OH$ | 224 | 2·224 | 0·455 | 4·88 |
| amyl $C_5H_{11}OH$ | 263 | 2·290 | 0·482 | 4·75 |
| amyl $C_5H_{11}OH$ | 348 | 2·482 | 0·695 | 3·57 |
| *iso* $C_5H_{11}OH$ | 270 | 2·315 | 0·4985 | 4·64 |
| *iso* $C_5H_{11}OH$ | 310 | 2·411 | 0·600 | 4·02 |
| $C_6H_5OH$ | 293 | 1·610 | 0·561 | 2·86 |
| $C_6H_5OH$ | 367 | 1·700 | 0·561 | 3·02 |
| $C_6H_5.CH_2OH$ | 380 | 1·842 | 0·558 | 3·03 |
| $CH_2OH$ | 295 | 1·884 | 0·565 | 3·33 |
| $CH_2OH$ | 308 | 1·898 | 0·591 | 3·21 |
| $CH_2OH$ / $CHOH$ / $CH_2OH$ | 306 | 1·795 | 0·576 | 3·12 |
| $C_2H_5 \rangle O$ | 182 | — | 0·514 | |
| $C_2H_5$ | 223 | 2·215 | 0·517 | 4·28 |
| | 271 | 2·305 | 0·523 | 4·40 |
| | 303 | 2·383 | 0·547 | 4·35 |

*Conclusions.*

1. On substituting an organic radicle for one of the hydrogen atoms in water, $p$ is considerably increased.

2. On graphing $p$ against absolute temperatures it will be seen that the curves of methyl, ethyl, propyl, butyl, and amyl alcohols are almost parallel to each other, especially in their latter portions, so that at any temperature common to all curves the increment in the value of $p$ due to $=CH_2$ is maintained. As we mount the series, the more polymerised is the alcohol at the melting-point; but at their boiling-points the values of $p$ are all approximately equal to 3+, compared with $p=2$ for water, and $p=4+$ for ether Thus,

$p$ (B.P.)

$\begin{matrix}H\\H\end{matrix}\rangle O$ ... ... ... 2·04

$\begin{matrix}C_2H_5\\H\end{matrix}\rangle O$ ... ... ... 3·09

$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\rangle O$ ... ... ... 4·35

3. The curves for *iso*-alcohols are below those for normal alcohols, but at the boiling-point they are very much alike (see Fig. 6).

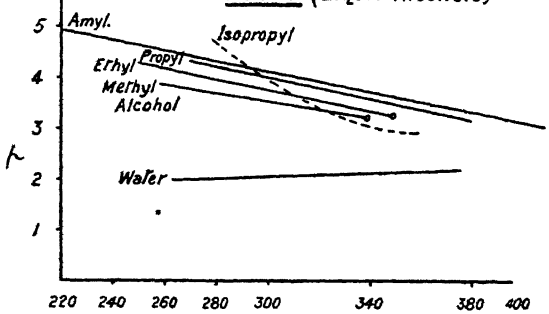



FIG. 6. (Liquid Alcohols)

TEMP

(In Fig. 6 "Isopropyl" should read "Isobutyl.")

4. The effect of substituting a second organic radicle in the water molecule (*e.g.*, to form an ether) still further accentuates the above changes.

5. The effect of introducing the hydroxyl group into the benzene ring or the side chain of an aromatic compound is to reduce *p* (compare with Nos. 1 and 4).

6. Glycol and glycerin are not so highly associated at the boiling-point as methyl alcohol, the first of the monohydric alcohols; neither are they so highly polymerised as the hydrocarbons from which derived.

| | | | |
|---|---|---|---|
| | $CH_3.H$ | $CH_3.CH_3$ | |
| | $CH_3.OH$ | $CH_2OH.CH_2OH$ | |
| | | | $CH_3.CH_2\ .CH_3$ |
| | | | $CH_2OH.CHOH.CH_2OH$ |
| T | 306 | 308 | 306 |
| *p* | 3·43 | 3·21 | 3·12 |

The results for a few fatty acids are given in Table X.

TABLE X.

| | Absol. Temp. | ST | Sobs | *p* |
|---|---|---|---|---|
| H.COOH (solid) | 273 | 1·025 | 0·430 | 2·38 |
| H.COOH (liquid) | 310 | 1·286 | 0·552 | 2·46 |
| H.COOH (liquid) | 330 | 1·309 | 0·515 | 2·54 |
| $CH_3COOH$ (solid) | 277 | 1·258 | 0·627 | 2·00 |
| $CH_3.COOH$ (liquid) | 308 | 1·572 | 0·5118 | 3·07 |
| $CH_3.COOH$ (liquid) | 323 | 1·591 | 0·537 | 2·96 |
| $C_2H_5.COOH$ ... | 343 | 1·808 | 0·536 | 3·37 |
| $C_2H_5.COOH$ .. | 351 | 1·811 | 0·560 | 3·23 |
| $C_3H_7$ COOH ... | 333 | 1·916 | 0·526 | 3·64 |

*Conclusions.*

1. Formic and acetic acids, and probably the other members of the series, too, follow the phosphorus curve on melting.

2. As we ascend the series there is a rise in the value of *p*, coinciding with an increase in the percentage of carbon (the most important polymerising element present) from 26 per cent in formic to 54 per cent in butyric acid.

3. For the acids included in this table, *p* is less than for the corresponding hydrocarbons from which they are derived, which contain much more carbon.

A few nitriles are dealt with in Table XI.

TABLE XI.

| | T | ST | Sobs | *p* |
|---|---|---|---|---|
| $CH_3CN$ ... ... | 321 | 1·746 | 0·541 | 3·22 |
| $C_2H_5CN$ ... ... | 330 | 1·880 | 0·538 | 3·50 |
| $C_3H_7CN$ ... ... | 340 | 2·111 | 0·547 | 3·86 |
| $C_5H_{11}CN$ ... ... | 359 | 2·264 | 0·542 | 4·17 |

*Conclusions.*

1. The nitriles are slightly more polymerised than the acids they yield on hydrolysis.

2. As the percentage of carbon rises from 58·8 ($CH_3$ CN) to 74·2 ($C_5H_{11}$.CN), *p* changes from 3·22 to 4·17.

Other well-known compounds are included in Tables XII.—XV.

TABLE XII.

| | | | | |
|---|---|---|---|---|
| $CH_3$ > CO $CH_3$ ... | 243 | 1·887 | 0·4825 | 3·91 |
| | 273 | 1·955 | 0·5064 | 3·86 |
| | 293 | 2·003 | 0·528 | 3·79 |
| | 303 | 2·024 | 0·5302 | 3·81 |
| | 333 | 2·075 | 0·5540 | 3·75 |
| $C_6H_5$.CO.$CH_3$ | 383 | 1·758 | 0·474 | 3·71 |
| $C_6H_5$ CO.$C_6H_5$ | | | | |
| ,, (solid) | 234 | 1·214 | 0·2300 | 5·28 |
| ,, (solid) | 295 | 1·257 | 0·3051 | 4·12 |
| ,, (liquid | 295 | 1·532 | 0·3825 | 4·00 |

The effect of nitration is shown in Table XIII.

TABLE XIII.

| | | | | |
|---|---|---|---|---|
| $C_6H_6$ (solid) ... | 273 | — | — | 3·64 |
| $C_6H_6$ (liquid) ... | 283 | — | — | 4·35 |
| $C_6H_6$ (liquid) ... | 367 | — | — | 3·94 |
| $C_6H_5.NO_2$ ... | 280 | 1·305 | 0·3524 | 3·70 |
| | 293 | 1·323 | 0·358 | 3·69 |
| | 366 | 1·400 | 0·402 | 3·48 |
| $C_{10}H_8$ (solid) ... | 318 | — | — | 4·13 |
| $C_{10}H_8$ (liquid) ... | 356 | 1·723 | 0·396 | 4·35 |
| $C_{10}H_8$ (liquid) ... | 368 | 1·733 | 0·427 | 4·06 |
| $C_{10}H_7.NO_2$ (solid) | 316 | 1·120 | 0·274 | 4·09 |
| $C_{10}H_7.NO_2$ (liquid) | 331 | 1·392 | 0·360 | 3·87 |
| $C_{10}H_7.NO_2$ (liquid) | 367 | 1·424 | 0·390 | 3·65 |

TABLE XIV.

| | | | | |
|---|---|---|---|---|
| $NH_3$ (solid) ... | 85 | — | — | 3·72 |
| $NH_3$ (liquid) ... | 273 | — | — | 3·05 |
| $C_6H_5.NH_2$ ... | 283 | 1·730 | 0·497 | 3·48 |
| | 366 | 1·846 | 0·538 | 3·43 |
| $(C_6H_5)_2.NH$ ... | 326 | 1·698 | 0·464 | 3·66 |
| | 339 | 1·714 | 0·482 | 3·56 |
| $C_6H_6$ ... ... | 283 | — | — | 4·35 |
| | 313 | — | — | 4·29 |
| | 367 | — | — | 3·94 |

There is a gradual gradation in the degree of polymerisation as we pass from $C_6H_6$ to $NH_3$.

The results for $CS_2$ are given in Table XV.

TABLE XV.

| | T | ST | S bs | *p* |
|---|---|---|---|---|
| $CO_2$ (solid) ... | 140 | — | | 2·82 |
| $CS_2$ (liquid) ... | 177 | — | | |
| | 243 | 0·432 | 0·2303 | 1·88 |
| | 273 | 0·449 | 0·238 | 1·88 |
| | 303 | 0·464 | 0·240 | 1·93 |

In Table XVI. I have compared my results with those obtained by other investigators. The following is the key to the Table:—

R.S. = Ramsay and Shield's original surface tension method.

R-R.I. = Rose-Innes' modification of the R.S. method.

B = Batschinski's ditto.

F = The present method.

TABLE XVI.

| Compd. | Temp | R.S. | R-R.I. | B. | F. |
|---|---|---|---|---|---|
| Water | 273 | 3·81 | 1·707 | 2·82 | 1·88 |
| | 373 | 2·66 | 1·405 | 1·10 | 2·04 |
| $CH_3OH$ | ?183 | — | 2·65 | — | — |
| | 280 | — | — | — | 3·64 |
| | 289 | 3·43 | — | — | — |
| | 293 | — | — | 3·43 | — |
| | 306 | — | — | — | 3·43 |
| | 339 | 3·24 | 2·17 | — | — |
| $C_2H_5OH$ | 183 | — | 2·03 | — | — |
| | 253 | — | — | — | 4·26 |
| | 289 | 2·74 | — | — | — |
| | 293 | — | — | 4·43 | — |
| | 313 | — | — | — | 3·61 |
| | 333 | — | — | 3·65 | — |
| | 351 | 2·43 | 1·46 | — | — |
| | 353 | — | — | — | 3·09 |
| $C_3H_7OH$ | 269 | — | — | — | 4·35 |
| | 290 | — | — | 5·03 | — |
| | 293 | — | — | — | 4·02 |
| | 340 | — | — | — | 3·56 |
| | 353 | — | — | 3·15 | — |

| | | | | | |
|---|---|---|---|---|---|
| $C_4H_9OH$ | 290 | — | — | 4·79 | — |
| | 340 | — | — | — | 3·56 |
| | 353 | — | — | 3·03 | — |
| $C_6H_5.OH$ | 275-293 | 1·01 | — | — | — |
| | 293 | — | — | — | 2·86 |
| $CH_3$ COOH | 289 | 3·62 | — | — | — |
| | 293 | — | 2·13 | 3·47 | — |
| | 308 | — | — | — | 3·07 |
| | 323 | — | — | — | 2·96 |
| | 373 | — | — | 2·74 | — |
| | 391 | 2·9 | 1·79 | — | — |
| $C_2H_5$.COOH | 289 | — | — | 2·48 | — |
| | 343 | — | — | — | 3·37 |
| | 351 | — | — | — | 3·23 |
| | 406 | — | — | 2·26 | — |

Here T=T

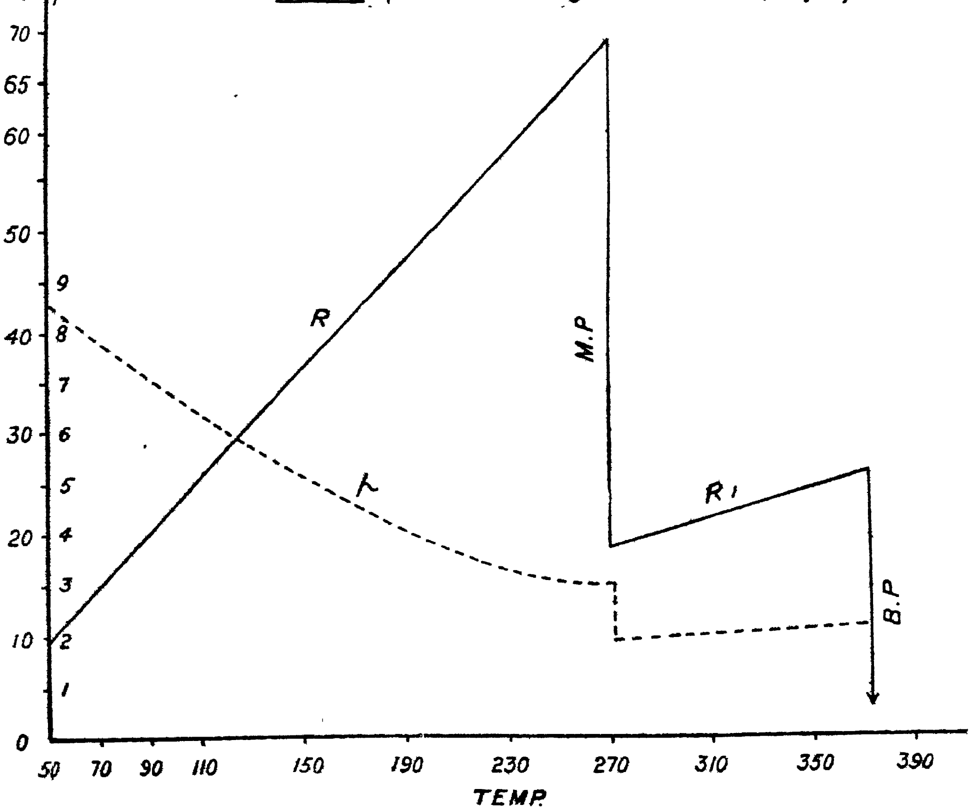
$$\therefore \frac{ps}{R} \cdot \frac{R_1}{p_1s_1} = \text{a constant}$$

$$\text{Now} \quad \frac{T+563}{37·7} = \sqrt{\text{Melticular weight}}$$

$$\therefore \left\{\frac{T+563}{37·7}\right\}^2 = R \times \text{average at. wt.}$$

$$\text{and} \quad \left\{\frac{T_1+136}{34·6}\right\}^2 = R_1 \times \text{average at. wt.}$$

FIG. 7 (To show change in value of $p$ & R)




Batschinski's and my results are often in close agreement, especially for the alcohols and acetic acid.

*Appendix.*

In the preceding paper nothing has been said about changes in the value of R (aggregations) on melting, &c., although changes in $p$ and $s$ have been noted. The vapicular weights were chosen without reference to the melticular weights.

At the M.P. (solid state)

$$\frac{T \times p \times s}{R} = k$$

——— (liquid state)

$$\frac{T_1 \times p_1 \times s_1}{R_1} = k_1$$

$$\therefore \frac{ps}{R} \cdot \frac{R_1}{p_1s_1} = \frac{ps}{p_1s_1} \left\{ \frac{\frac{T_1+136}{34·6}}{\frac{T+563}{37·7}} \right\}^2 = \text{a constant}$$

$$= \frac{ps}{p_1s_1} \left\{\frac{T_1+136}{T+563}\right\}^2 = \text{a constant}$$

Substituting the values for water we can find the constant and then $R_1$ with respect to R at the M.P. For water :—

$$ps = 1·5$$
$$p_1s_1 = 2$$
$$T = 273$$

$$\therefore \left[\frac{T_1+136}{T+563}\right]^2 = \left[\frac{409}{836}\right]^2 = \frac{1}{4 \cdot 178}$$

$$\therefore k^{273}_{water} = 0 \cdot 191$$

Keeping R for ice at $273° = 69$

$\therefore$ $R_1$ for water at $273° = 17 \cdot 5$

In Table III., $R_1$ for water at 273° was 23·3.

$\therefore$ to get $R_1$ in the liquid state, relative to the value in the solid state, multiply the values previously obtained for liquid state by $\frac{17 \cdot 5}{23 \cdot 3}$ or 0·751.

*E.g.*, $R_1$ for bromine at 302° was taken as 2, $\therefore$ if $R=5$ for bromine at its M.P., $R_1$ at $302 = 2 \times \frac{17 \cdot 5}{23 \cdot 3} = 1 \cdot 5+$

If R or $R_1$ for any substance came to less than the number of atoms in the compound (or one, if an element), all values of R and $R_1$ must be raised to give these minimum values. The changes in the aggregations for water are shown in Fig. 7.

## THE PHYSICAL PROPERTIES OF THE SOIL IN RELATION TO SURVEY WORK.*

By G. W. ROBINSON, M.A., Adviser in Agricultural Chemistry University College of N. Wales, Bangor.

CONSIDERABLE difficulty has been experienced in the correlation of plant and soil surveys. This may be attributed to a large extent to the defects of existing methods of soil classification. In the classification of any material, whether soils, plants, or animals, the method to be adopted is to a large extent arbitrary. For example, soils may be classified on a purely genetic basis, and, from the geological point of view, this classification is the one naturally to be adopted. From the point of view of plant physiology, however, a genetic classification may be of little use.

In many regions the genetic classification proves quite satisfactory even from the point of view of plant physiology, and the properties of a soil may be closely correlated with the conditions of its origin. Geology and climate are the principal factors in soil formation. Under conditions such as obtain over most of England and Western Europe generally, the influence of geology on soil is well exemplified. Hall and Russell, in their survey of the soils of Kent, Surrey, and Sussex, were able to classify soils satisfactorily on a geological basis. Under more extreme conditions of climate as exemplified by the semi-arid regions of South-Eastern Europe, and the extreme humid regions of our own islands, the influence of geology on soil is much less marked. Accordingly we find the Russian school of soil workers classifying soils largely on a climatic basis.

Working in North Wales, the writer has found the correspondence between geology and soil much less marked than in England. The rather extreme humid conditions may account for this to a large extent. Other observers have noted that under extreme conditions of climate, whether of temperature or rainfall, the influence of the parent rock is reduced to a minimum. The lack of correlation between geology and soil need not, however, prevent the investigator from establishing soil types. The question, of course, arises whether soil types always exist or whether in some cases soils are unclassifiable. In some districts the isolation of soil types is an impossible task. Among the glacial soils of certain districts of North Wales it is possible to find a continuous gradation from sands to clays without any definite grouping. In other areas soil types do undoubtedly exist, and a large number have already been described.

This leads to the question of the criteria used in soil classification and the isolation of soil types. At present, mechanical analysis is the general criterion used for the characterisation of soils. In this country the soil is separated into six grades of particles, varying from fine gravel to clay. There are, however, throughout the world, a large number of different conventions as to the limits of the size of the different fractions. Uniformity is impossible, as each country has accumulated too many data to effect a change. It is thus impossible to compare an English soil with, say, a Hungarian or a Swedish soil. Even in the case of the clay fraction where the upper diameter limit is taken as 0·002 mm., any comparison is vitiated by the different methods of separation in use. Another drawback to mechanical analysis namely, the discontinuity of grouping, has been overcome by the elegant apparatus devised by Sven Odèn, whereby the mechanical analysis of a soil can be expressed as a continuous curve.

The main defect of mechanical analysis, however, as a basis for soil classification, is that it only gives information as to the properties of the soil by inference. The mechanical analysis will tell us little about the properties of the soil beyond what is contained in the practical man's classification into sands, loams, and clays. Indeed, within certain limits, the same information might be gleaned by the ordinary methods of silicate analysis. In other words, the information given by mechanical analysis only differs in degree from that given by chemical analysis. The formula of an organic compound describes its constitution, but its properties are given by such constants as melting-point, boiling-point, and refractive index. The mechanical analysis of a soil is analogous to the constitutional formula of an organic compound.

Mechanical analysis is of undoubted value from the point of view of the genetic classification of soils. It enables the investigator to group together soils of similar origin. Apart from its diagnostic value, it gives certain indications as to the actual properties of the soil, but these are only imperfect and indirect. Attempts have been made to correlate cropping with mechanical analyses. The correlation is, of course, complicated by climatic and economic factors, but even allowing for these, the correlation obtained is imperfect, and it may be doubted whether the mechanical analysis of soil can do more than standardise the practical man's classification of soils into heavy, medium, and light.

It is probably this defect in mechanical analysis which is responsible for the disappointing results obtained from soil surveys. Soil survey work has been in progress in this country for 15 years or more, while ecological studies have been carried

* A contribution to a General Discussion on "Physico-Chemical Problems relating to the Soil" held by The Faraday Society, on Tuesday, May 31st, 1921.

on for an even longer period. Yet the actual progress in the correlation of plant and soil surveys is almost negligible.

In North Wales one frequently finds tracts where the edaphic conditions as indicated by the natural vegetation vary sharply from point to point without any apparent change of soil type. Differences in the air and water conditions of the soil are probably the main factors causing these variations, but there is no reliable quantitative method of expressing them. The mechanical analysis is almost useless, and can only occasionally be correlated with the natural vegetation. I am speaking, of course, of a province where the climatic conditions are somewhat extreme, but the same difficulty must frequently arise in districts of more moderate rainfall.

In the opinion of the writer, the only remedy for this, and the only way to get a fresh impetus for the field study of soils is to examine the soil from the point of view of its actual properties. To say that a soil contains 20 per cent of clay does not give a picture of the actual properties of the soil except by inference. In fact, certain materials, such as kaolin and finely ground slate, give as much clay by mechanical analysis as fairly heavy soils, although they lack the characteristic property of clays, namely, plasticity. Further, among the plastic clays, the amount of clay by mechanical analysis cannot be correlated completely with the texture.

Although the original data of mechanical analysis are quantitative, the deductions from them are certainly not quantitative. The most valuable data about the soil are those which give direct information as to the properties of the soil as they affect plant life. In the opinion of the writer, the data in question would be given by a series of physical constants comparable to those which are indispensable to the description of a newly-discovered element or compound.

An example of this method of investigation is furnished by Atterberg's work on the plasticity of soils. From the agricultural point of view, information as to the working properties of a soil is highly desirable, and the figures given by Atterberg's methods are of direct importance. His "Plasticity Number" gives the range of water content over which a soil is plastic, while the figures obtained by him for the cohesiveness of soils (festigkeit) give direct information as to the resistance of the soil to comminution by the ordinary operations of tillage.

Pore space as a physical constant for the soil would be of considerable use. Owing to the difficulties of obtaining a sample of the soil without disturbing its field structure, a satisfactory routine method for determining this value has not been devised. The methods of Kopecky and Trnka are instances of attempts to solve the problem. Could a satisfactory method be devised, it would be easy to determine to what extent it is specific for a given soil, and to follow the variations due to season and soil treatment.

Closely connected with pore space is the determination of water-holding capacity. Here again, some confusion reigns, partly due to the same difficulty of obtaining a sample with unaltered field structure. A constant to represent the permeability of soil for water and air would be of considerable value. Green and Ampt's methods, if they could be applied to investigation of natural soils, would be very suitable. The specific surface of soils has undoubtedly a physiological significance as a measure of the degree of dispersion. The methods of Mitscherlich, Hilgard, and others, for the measurement of hygroscopicity are worthy of attention, and it ought to be possible to devise some rapid routine method applicable to the study of soils on an extended scale. The problem has also been attacked by measuring dye absorption In the opinion of the writer this method is not to be recommended, as it is liable to be complicated by chemical reactions between the dye used and soil constituents.

There are, of course, other physical properties of the soil on which quantitative ideas are needed, and it is to be hoped that the recognition of soil physics as a branch of investigation at Rothamsted will lead to a useful development of the work begun in this country by Warrington.

Whatever physical measurements may be devised for the investigation of soils, there are certain desiderata if they are to be of use in field study. Firstly, they must deal with the soil in its natural structure. The soil of the laboratory is an artificial product. Results obtained on it are apt to be misleading on the chemical side, and even more so on the physical side. The methods devised should also be capable of being repeated in large numbers. The soil is such a complicated object of study that statistical methods have to a large extent to remedy the unreliability of single observations. Methods to be devised for the physical investigation of the soil may have to sacrifice a little accuracy in order to make it possible to multiply observations in large numbers for the purposes of statistical treatment.

If reliable methods could be devised for characterising the physical properties of soils by a series of physical constants, the edaphic classification of soils might be placed on a much surer basis than at present and correlation with vegetation and agricultural conditions might be expected. The physical properties of a soil as expressed by such a series of constants would be of importance from the point of view both of plant physiology and of practical agriculture, since they would give quantitative expressions for factors which directly affect edaphic and cultural conditions. Supplemented by a few chemical and economic data, the agricultural properties of a soil could be completely characterised.

The investigation of the physical properties of the soil must in future be one of the most promising lines of inquiry. The soils of our country do not, as a rule, show any striking deficiencies in plant food capital and such deficiencies as do occur are easily made good The ultimate productiveness of our soils is largely a matter of physical properties. With the new impetus given to the physico-chemical study of soils, of which this discussion is an evidence, it may be expected that the routine methods in use by field investigators will be more in the nature of physical determinations than of chemical analyses.

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ROYAL INSTITUTION.—The General Meeting of the Royal Institution will be held on Monday, July 4, 1921, at 5 o'clock.

## RUBBER RINGS IN CONNECTION WITH TEST-TUBES.

The placing of a rubber ring around a test-tube about 1in. from the mouth has many advantages, as well as rendering the test-tube less liable to breakage in washing, knocking together, &c.

Having all my test-tube stands in use, and wishing to keep several others in a vertical position, the difficulty was soon overcome by driving one or two nails or long pins into the edge of a shelf and supporting the test-tubes in between the nails, as in Fig. 1.

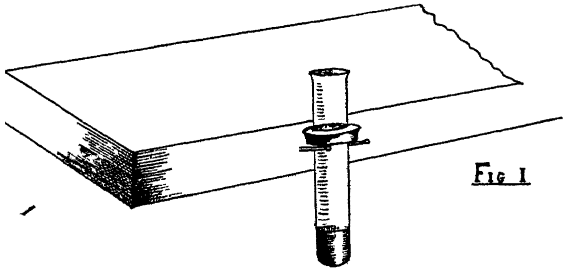

Fig 1

The use of a rubber ring on a test-tube has many other advantages, two of which are as follows:—

1. The tube can, if desired, be laid down on a bench (assuming, of course, that it is not too full) without losing any of the contents (see Fig. 2).
2. The ring permits the test-tube to be held in the fingers while very hot, during boiling processes, &c. The tube may also be supported by a hole in the shelf.

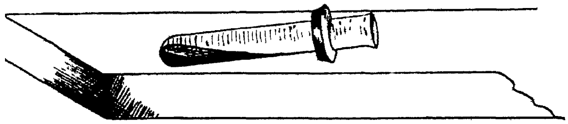

Fig 2

These rings are easily obtainable in all sizes, and should be about ⅛in. in thickness.

W.K.F.

## NEW BRITISH CHEMICAL STANDARD.
### Hematite Iron "B".

This standard, which is now available, has been prepared under the auspices of a body of analysts in order to meet a long-felt need in settling disputes as to the amount of phosphorus, sulphur, &c., in the purer varieties of hematite iron, as explained in a paper in the *Proc. Clev. Inst. Engineers* (*Middlesbrough*), No. 4, February, 1920.

The analytical standardisation has been carefully undertaken by a selection of experienced chemists representing all the chiefly interested parties, viz., one Government laboratory, three special hematite iron makers, four special hematite users, three independent analysts, and the U.S. Bureau of Standards.

The analysis is as follows: phosphorus 0·025 per cent; arsenic 0·031 per cent; sulphur 0·031 per cent; and titanium 0·108 per cent.

The standard may be obtained either direct from Organising Headquarters, 3, Wilson Street, Middlesbrough, or through any of the leading laboratory furnishers at a price just sufficient to cover the cost. A certificate, giving the names of the analysts co-operating, the types of methods used, and a detailed list of their individual figures, will be supplied with each bottle.

## RADIUM.*

*Chemical Effects of Radium Emanation.*

Dr. Lind is conducting a new series of experiments on the chemical effects of radium emanation in gas reactions. Improved apparatus was installed for eliminating hydrogen and oxygen gases from the emanation with additional equipment for final purification by liquid air. In a study of the combination of hydrogen and oxygen produced by $\alpha$ particles, it was discovered that the recoil atoms also produce chemical action proportionate to the ionisation.

*Redetermination of the Spectrum of the Radium Emanation.*—In co-operation with Prof. R. E. Nyswander, of Denver University, Dr. Moore and Dr. Lind continued the work of redetermining the spectrum of radium emanation. A number of lines have been successfully photographed and measured, and their identiy as part of the spectrum has been established with certainty; some of these coincide with the principal lines observed by other authorities, and the rest are apparently new lines.

Some work was also done in photographing the spectral lines of krypton and zenon furnished and purified by Dr. Moore.

*Redetermination of Radium-Uranium Ratio.*—Dr. Lind, of the station, and Prof. L. D. Roberts, of the Colorado School of Mines, concluded their investigation on the redetermination of the radium-uranium ratio, which they found to be $3{\cdot}40\times10^{-7}\pm0{\cdot}03$. Results were published in June, 1920, number of the *Journal of the American Chemical Society*.

Dr. Lind also prepared the third section of a series of papers on methods of determining radium, published in the *Journal of Industrial and Engineering Chemistry*. The paper deals especially with improvements in electroscopes in recent years, and use of the X-ray electroscope in examining radioactive ores and other radioactive products.

*Radium Fractionation.*—Dr. Moore and Dr. Lind assisted the officials of the Minerals Recovery Co., of Denver, in overcoming difficulties they have experienced in radium fractionation. This company purchased and is operating the plant for treating carnotite ores built by the National Radium Institute.

*Luminous Paints.*—Experimental study of the properties of radium luminous paint continued throughout the year. Photometers for luminosity measurements were standardised, and a table prepared to convert the readings in centimetres into microlamberts.

A method was worked out for the preparation of pure zinc sulphide, and a quantity of the pure nonluminous salt was obtained. The action of radium emanation on the pure salt is being studied and this study will be continued on the prepared phosphorescent material.

*Extracted from the Tenth Annual Report of the Director of the Bureau of Mines, U.S.A., for year ended June 30, 1920.

## ON CHEMICAL AFFINITY.

By A KOREVAAR.

When we peruse the chemical literature and notice the meaning of the word affinity, it soon becomes clear that two different things are called by this name. In the first place, we know the classic definition of affinity coming from the Greek philosophers, and which denotes a force, acting between combining atoms In the second place, modern chemistry shows us the thermodynamical conception of affinity, created by van't Hoff, which defines affinity as the maximum external work done by the chemical reaction at constant temperature and volume.

We, therefore, find the chemists using two quite different definitions of chemical affinity. It is to be expected that such a state of affairs will cause a confusion in our science, and this is really the case The different text-books on chemistry define affinity quite differently. One maintains the classical definition, a second gives the thermodynamical one, and others mix both definitions up in a wonderful way, some even advocating removing this vague idea from chemical science

This last would not be right. Neither the classical nor the thermodynamical conception is indefinite; but we must always remember that the word affinity denotes two quite different ideas. At present this is not generally known. This appears clearly from the confusion on this point, existing in our text-books, as shown by the following examples:

Lewis, in his "A System of Physical Chemistry," 1920, ii., 339, gives the definition by van't Hoff; Holleman, in his text-book of inorganic chemistry, 1906, p. 47, the classical conception. Ostwald, in his "Grundlinien der anorganischen Chemie," 1904, p. 88, discusses the classical conception and advises not to use this idea, because he thinks it in contradiction with certain phenomena which, on p. 104 appear to be the reversible reactions.

J. W. Mellor, in his "Modern Inorganic Chemistry," 1912, p. 94, deals first with the classical conception, but does not stick to it further on, while R. de Forcrand, in his "Cours de Chimie," 1919, does not speak at all about affinity.

Ostwald's attitude in his "Der Werdegang einer Wissenschaft," 1908, is quite remarkable. In this book, Chapter VI deals with affinity. In fact, in the beginning the author writes about affinity, but soon he enters into thermodynamical considerations without giving an analysis or description of the idea "affinity," and the reader gets the impression that the author does not know what he shall say on this point.

The cause of all this is quite clear. The authors are not conscious that two different ideas are called by the same name "affinity."

We hope that this short explanation may cause the different authors to revise their texts on this point, and that they will not only rigidly separate the classical from the thermodynamical conception; but also that they will call these different ideas by different names. The best were perhaps to continue to call the classical conception by the name "affinity," and to denote the thermodynamical one by the maximum external work of the reaction.

O. Sackur ("Die chemische Affinität und ihre Messung". Vieweg, 1908) has contributed to a great extent to the existence of the abovementioned confusion. His book on chemical affinity is well known and justly admired, as it gives a clear and simple treatment of the maximum external work, and its applications to chemistry. But this author has totally forgotten that the classical conception of affinity has still a right to exist. Sackur begins in the first chapter with a historical development of the idea of affinity, and we might expect that, in doing this, he would have discovered the confusion of ideas in question But the author has failed to do so, and therefore it is worth while to trace the historical line once more and show how it has been possible that chemical science gave birth to two different definitions of chemical affinity.

We may say that the conception of affinity as a force between the smallest particles, or in the middle ages, when the atomic theory was denied on the authority of Aristotle, as a force between the elements, remained invariably the same till the end of the 18th century. It is true that the nature of these forces was differently explained. The Greeks had an antropomorphistical conception of affinity, and this character was preserved till the 17th century. The force, driving different substances together, was compared with love between two human beings. With the rise of the mechanical contemplation of nature in the 17th and 18th centuries, the ideas on the nature of chemical force became more sober. Lemery (1675) thought the atoms were provided with little hooks for sticking to each other. Newton classified the chemical force under the gravitation of the smallest particles; but according to him it was not necessary that this force was, as with visible masses, inversely proportional to the distance. This latter restriction was dropped by Buffon (1770), who saw no difference between chemical force and gravitation.

In all of these theories the driving force of a reaction was considered acting between the smallest particles of the combining substances. The difficulties arose when Berthollot proved experimentally that the progress of a reaction not only depends on the nature of the reacting substances, but also on their quantity, or, as Guldberg and Waage proved afterwards, on their concentration. These researches led, in 1864, to the formulation of the law of mass action. Guldberg and Waag's views are of the greatest importance for our purpose, and so we will pay some further attention to them

Guldberg and Waage published their views in three treatises, which are collected in Astwald's Klassiker, No. 104, under the title. "Untersuchungen uber die Chemischen Affinitaten" The treatises are dated 1864, 1867, and 1879, and we are not surprised that the ideas of the authors have developed in that course of time. In fact, we shall see that their conception of chemical affinity has undergone radical changes. Their views may be summed up as follows:

A substance A and a substance B combine, by the operation of cohesive forces between the molecules, to a compound AB. When a substance C reacts with AB according to the equation

$$AB+C=AC+B,$$

then, AC is principally produced by cohesive forces between A and C. But the forces between A and B, and perhaps also between B and C, have

all excited their influence on the reaction, so that the force that finally produces AC is the result of the co-operation of different forces. This resultant force $k$ is the coefficient of affinity. According to these investigators, the driving force of a reaction is not only proportional to the coefficient of affinity, but also to the concentrations of the reacting substances. While formerly only the affinity was considered to be the driving force of a reaction, according to the new conception, the affinity is only a part of the driving force. *The affinity has to be distinctly distinguished from the driving force of a reaction, they are quite different things.*

Guldberg and Waage expressed the driving force of a reaction by the product of the concentrations of the reacting substances and the coefficient of affinity $k$. When these concentrations are denoted by $p$ and $q$, then the driving force $= kpq$. The authors originally thought that in determining $k$, they had found a measure for the affinity, for $k$ was the resultant of the forces, acting between the molecules; but on this point they changed their views fundamentally. This appears form their treatise of 1879, where the idea of mobile equilibrium is developed in the following way.

To explain a reaction according to the equation:

$$A+B=A'+B',$$

it is insufficient to accept cohesive forces between the molecules, but it is also necessary to keep account with the motion of the atoms and molecules. The equilibrium is not a state of repose, it is a mobile equilibrium, the reactions in both directions going equally fast. The authors give a sketch of a kinetical deduction of the law of mass action. If $p$ and $q$ are the number of molecules of A and B in the unit of volume, then the number of collisions between the molecules A and B is represented by the product $pq$. When each collision caused a reaction, the reaction velocity would be $=Qpq$, Q being a velocity coefficient, dependent on temperature. Of $p$ molecules of A, only a part $a$ will be in a condition to cause a reaction during a collision. Of $q$ molecules of B, a part $b$ is in a similar condition. So that $ap$ molecules of A will combine with $bq$ moleules of B, and the reaction velocity is: $Qapbq$ or $kpq$ when $k=Qab$. It is clear that this formulation is based on a quite different conception of $k$. At present this constant $k$ is the product of a velocity coefficient Q and two constants $a$ and $b$, which are perhaps best called activity coefficients. For the present it is impossible to determine these constants separately.

Concerning their views on chemical affinity, we conclude from their treatises the following: Guldberg and Waage certainly adopt the classical idea of affinity, viz., the affinity being a force acting between the molecules. This is clear from their former treatise, and appears in the mathematical treatment of the problem from the meaning of $k$. Their later considerations about the mobile equilibrium do not contradict the classical definition of affinity, but the meaning of $k$ has become much more complicated and their conception of affinity is not clearly defined. The great importance of Guldberg and Waage's work does not lie in the sphere of affinity, and their great success is due to the formulation of the law of mass action, which became the basis of chemical statics and dynamics. At present, the names of these investigators are always connected with the law of mass action, but never with chemical affinity, though this was originally the object of their researches.

Though they did not do it themselves, and though, as far as we know, others did not do it either, we may draw from Guldberg and Waage's treatises a conclusion of importance. We have learned to make a sharp distinction between affinity as a force, acting between the smallest particles and the driving force of a reaction. This is clearly expressed in their original formula

$$\text{Driving force}=kpq.$$

The driving force of a reaction is quite different from the affinity.

Though we are convinced that $k$ is in some way connected with the affinity, it appears from the later treatise of Guldberg and Waage that this connection is not a simple one. It is true that they succeeded in determining $k$, but the ydid not know the exact meaning of $k$. This is the reason that all determinations of affinity have failed.

In 1883, van't Hoff showed that the driving force of a reaction can be measured by the maximum external work at constant temperature and constant volume which is done by the system in passing from the initial state to the equilibrium point. This thought has been of the greatest importance for chemical science, but it was a great pity that van't Hoff called the driving force a reaction, affinity ("Vorlesungen über theoretische und physikalische Chemie," 1901, i., 171) and in consequence, considered the maximum external work of a reaction a measure for affinity.

In the preceding pages we have emphasized the difference between the driving force and affinity. By calling the driving force, affinity, van't Hoff has made the clear distinction between these two different ideas very vague. This was unnecessary. The maximum external work is a sharply defined idea, which does not need any other name, and it was a pity, for it caused a confusion, which, as we have seen, remains in our text-books up to the present day.

After this digression we return to Sackur's historical treatment of affinity. Sackur did not understand the confusion of affinity and driving force. According to him, the thermodynamical conception of affinity has gradually developed from the classical one. If this were true, the modern formulation would have made the ancient one superfluous, for then the modern one, by a broader development of the idea, would have opened a new insight, given us a new view-point, which would have included the old one completely. This did not happen, and Sackur writes unjustly that van't Hoff succeeded in *"eine gluckliche Definition der Affinitätskraft aufzustellen, die allen bisherigen Erfahrungen Rechnung trägt und gleichzeitig die quantitative Messung in mechanischen Massen ermöglicht."*

No, van't Hoff has mixed up the ideas of driving force and affinity; but, by calling the driving force affinity, the classical idea of affinity does not become superfluous. Therefore it is not true that van't Hoff's affinity, as Sackur says: *"allen bisherigen Erfahrungen Rechnung trägt."*

It is better that the maximum external work of a reaction remains the maximum external work. Then, it is clear to everybody that the affinity is not meant. That is the question, and as Sackur

did not understand it, his much-read and otherwise excellent book is also responsible for the confusion which prevails in this sphere of chemical science.—*Journal of Physical Chemistry*, April, 1921.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

*Ordinary Meeting, June 16, 1921*

PROF. C. S. SHERRINGTON, President, in the Chair.

THE following papers were read:—

*"Velocity of Sound in Gases at High Temperatures, and the Ratio of the Specific Heats."* By H. B. DIXON, F.R.S., COLIN CAMPBELL, D.Sc., and A. PARKER, D.Sc.

*"The Ratio of the Specific Heats of Air and of Carbon Dioxide."* By J. R. PARTINGTON, D.Sc.

The ratio of the specific heats, $\gamma = c_{-p}/c_{-v}$, has been determined by the method of adiabatic expansion for the gases air and carbon dioxide. The gas was contained in a 120-litre vessel, and the temperature change immediately after expansion followed by a platinum thermometer, with compensating leads of wire 0·001 mm. diameter, the resistance of which was observed by an Einthoven string galvanometer of 0·01 seconds period The fundamental temperature measurements were made by a mercury thermometer. The results were calculated by the characteristic equation of D. Berthelot, so that deviations from the ideal gaseous state were allowed for. The final results, which are believed to be accurate to 1 part in 1000, are: $\gamma$ for air at 17° C. = 1·4034; $\gamma$ for carbon dioxide at 17°C. = 1·3022. From these numbers the specific heats of the gases were calculated by Berthelot's equation, with the following results: $c_{-p}$ for air at 17° C. = 0·2387 cal.; $c_{-p}$ for carbon dioxide at 17° C. = 0·1996 cal. All the values refer to atmospheric pressure.

*"'Light Body' Hydrophones and the Directional Properties of Microphones."* By A. B. WOOD, D.Sc., and F. B. YOUNG, D.Sc.

Prof. W. H. Bragg's theory of the vibration under water of a rigid body of low density has been tested. It is found that a light prolate ellipsoid actually possesses directional properties by virtue of its shape. Quantitative results obtained agree with calculated values supplied by Prof. Lamb.

Owing to the pronounced intrinsic directional properties of the microphone (when suitably mounted), a spherical "light body" hydrophone is practically equal in directional efficiency to one of ellipsoidal form.

Though "light body" hydrophones are not so sensitive as hydrophones of other types, a miniature spherical one proved of great value as an experimental exploring instrument.

*"Acoustic Disturbances produced by Small Bodies in Plane Waves transmitted through Water, with Special Reference to the Single Plate Direction Finder."* By A. B. WOOD, D.Sc., and F. B. YOUNG, D.Sc.

The experiments were undertaken primarily with the object of elucidating the action of the "single plate direction finder"—an instrument designed for detecting the direction of a source of sound submerged in water.

Sound distribution was explored round a number of discs immersed at a distance from a small submerged source of sound. By means of a pair of miniature hydrophones—one bi-directional, the other non-directional—it was possible to chart (1) direction of oscillation of the water particles; (2) relative amplitude of the movements; (3) relative amplitudes of the pressure oscillations.

The charts obtained fall broadly into two classes, according as the discs are solid or contain air-filled cavities, very minute air-filled spaces giving marked effects. Charts are shown of sound distribution round both the bi-directional and the uni-directional direction finders.

The behaviour of a typical baffle-plate is investigated. No satisfactory theory of the baffle can be offered to cover all experimental facts.

An Appendix deals with the exploration of the acoustic field produced on the reservoir by a small source of sound.

*"Some Problems connected with Evaporation from large Expanses of Water."* By M. A. GIBLETT.

The water which falls as rain, &c., is originally evaporated from the earth's surface, in particular from the oceans. It is therefore important to ascertain how the evaporated water distributes itself in an atmospheric current during its progress across a water-surface, and how the amount of water rendered available depends on the length of the path over the surface and on meteorological conditions.

These problems are considered for a current of air of uniform speed, moving over a water-surface of uniform temperature. In the immediate vicinity of the surface is a thin layer of air through which water-vapour diffuses slowly by molecular processes, but above this is a rapid transition to a turbulent *régime*, where diffusion becomes much more rapid. Account is taken of the complex molecular processes at and near the water-surface, by means of an empirical evaporation formula, and the problem is treated as one of eddy-diffusion with this as boundary condition.

Formulæ are obtained for humidity at any point of the air-current, and for rate of evaporation from stretches of water extending any distance downwind. Introducing numerical values for the constants in the empirical formula, the distribution of water-vapour is obtained for some typical cases, and an estimate made of the rate of evaporation from long stretches of water under various conditions of wind, water-surface, temperature, and turbulence. The formulæ are employed to examine the nature and magnitude of the effect which each of the last-mentioned elements may exert, when varied within their natural range, and to compare the evaporation under different sets of possible conditions. The results emphasize, amongst other things, the control exercised by atmospheric turbulence over evaporation from large areas.

*"The Photographic Efficiency of Heterogeneous Light."* By F. C. TOY, M.Sc., A.Inst.P.

This paper investigates the question of the action of heterogeneous light on the photographic plate. Two possible laws of action are discussed:—

(1) All the different radiations composing the heterogeneous beam may act simultaneously but independently, *i.e.*, each may act as though the

others are not present.

(2) All radiations may act simultaneously, but not independently.

This question is investigated theoretically, and it is shown that the possibility of testing it experimentally depends on the form of law connecting the probability of a single grain of the photographic emulsion being made developable with the intensity of the exciting light. The form of this law, recently proved experimentally by Slade and Higson, is considered, and a result is deduced which can be directly tested by experiment. From the evidence thus obtained it is concluded that over the spectral range used in the experiments ($\lambda 4350$ to $\lambda 4000$) radiations of different frequencies do not act independently in producing the photographic effect, but simply as a total amount even when a difference in quality exists.

## NOTICES OF BOOKS.

*Famous Chemists: The Men and Their Work.* By Sir WILLIAM TILDEN, F.R.S., D.Sc., LL.D., Sc.D., Professor Emeritus of Chemistry in the Imperial College of Science and Technology. London: George Routledge & Sons. New York: E. P. Dutton & Co. 1921. Price 12s. 6d. net.

THE above work by Sir William Tilden is not a history in the usual sense of the word, it is rather a series of sketches collected with much apparent care of the lives of many men of the past whose names and work are familiar enough in the scientific world, and well-known to the educated public. The work is of peculiar interest, for the author has related in a very charming manner many details in the lives of those great men of whose labours we are reaping the fruit, while he has unconsciously added not a little of his own personality. As a result, the book has a fascination that those who know the author can very fully appreciate.

Sir William, in arranging the material for his book has taken for a guiding principle the Evolution of the Atomic Theory from the early idea of the chemical element, the Laws of Combination, Application of the Atomic Doctrine to the explanation of chemical phenomena, the application of the idea of Valency to the constitution and structure of the Molecule, and the study of the Properties of Atoms. The men whose lives are recorded are those who have taken a leading part in researches in this domain.

The material of the work is arranged in ten groups, commencing with Robert Boyle as the father of chemistry in 1691, through the period of the Phlogistians, to Scheele in 1786, and then on to the Anti-phlogistic Revolution in 1794, where we have the melancholy history of Lavoisier told with a pathos that enhances the interest in one of the saddest deeds of the French Revolution; the account is so vividly told that in reading it one seems to be carried back into the scenes of that very dark time. The animosity of Murat brought about by the fact that he once attempted to make himself prominent in connection with physical science and had propounded a "Theory of Fire" that was condemned by Lavoisier in no measured terms—the disgraceful behaviour of the chemist Fourcroy—the lodgment in the Port-libre prison—the frantic efforts of his devoted wife to obtain his release—the pathetic letter that he wrote to her begging her not to exhaust herself in useless efforts, and the last scene, when, having first witnessed the end of his friend and father-in-law Paulze, he was placed under the axe, constitute one of the saddest pages in human history. "The world has seen many revolutions since that day, and other revolutions will arise so long as injustice continues to be imposed by the few on the many"

The application of Electricity to the service of Chemistry is introduced by a clearly-written biography of Sir Humphry Davy, which is very fully illustrated; the Poet-Chemist seems to live again, and in reading the account one passes from one place to another in the life of this remarkable man with an interest that makes it difficult to lay the book aside; in these days of after-war darkness, with strikes, labour troubles, murders, and the nauseating activity of the divorce courts, it is interesting indeed to follow the mind of Davy in one of his early poems.

Is this a time of minstrelsy,
  When Nature rests in deathlike sleep,
And roots and buds and herbage lie
  Embalmed in cerements deep.
It is a time of minstrelsy,
  For round these walls what magic forms
Appear in grace and harmony,
  The pencil of the artist warms
The coldest scenes and powers sublime,
  Awakening moral forms of things,
And new creations steal from Time
  His scythe, and close his wings.
It is a time of minstrelsy.
  For social converse wakes the mind
To pure and happy sympathy;
  And elegance and taste refined.
Call to the hospitable board
  The force of reason, and the flow
Of memory with wisdom stored
  Which might awake a grateful glow
In Fancy e'en though checked by age.
  Make sunshine in the darkest day,
And kindle in the coldest sage
  Some strain of vocal minstrelsy

Many illustrations are given, including the humorous sketch of the Theatre of the Royal Institution by Gillray, where Davy, acting as assistant, is seen administering a dose of some gaseous compound to a trustful member of the audience

The life history closes with a reproduction of the tomb of Davy in the cemetery of Geneva.

The life of Faraday falls on to Group VI., "Electro-Chemistry," and there is to be found a fund of information that fails in interest only by the fact that the history has been written so frequently.

In the chapters headed "Molecules and Atoms Defined" are to be found the lives of Avogadro and Cannizzaro, followed by Liebig, Dumas, Frankland, and Williamson, and the last groups are devoted to Mendeleeff, Crookes, and Ramsay.

The life and work of Crookes is given in great detail, accompanied by a good recent portrait that was taken in his study, together with several photographs of the Laboratory in Kensington Park Gardens; the account is strictly accurate, as can be vouched for by the writer, who acted as his private assistant from 1881 until his death. Sir William Crookes was very retiring, and but little is known of his private life.

The life of Ramsay has more the character of narrative than that of Crookes; the brilliant researches that led to the discovery of the inert

gases of the atmosphere are in themselves sufficient to fill a volume, and indeed that has already been done by Sir William himself in his "Gases of the Atmosphere." In the sketch before us, the life and the work of the man are happily blended together, and the reproduction of some letters written from Bombay and on board ship on the occasion of an official visit to India are full of human interest and touches of humour that will be prized by those who had the pleasure of his acquaintance.

The book ends with an "Epilogue" in which the recent developments in chemical theory brought about by the demonstration of the properties of radioactive matter are briefly reviewed.

The work is certainly one of the most interesting that has appeared since the war, and by its publication the author has brought a real pleasure within the reach of all lovers of pure science, and many a tired one will be grateful for a few hours' quiet spent over "Famous Chemists: The Men and their Work."

J.H G.

*Bibliotheca Chemico-Mathematica Catalogue of Works in Many Tongues on Exact and Applied Science.* With a Subject Index compiled and annotated by H.Z. and H.C.S. With 127 plates, containing 247 Portraits and Facsimiles. Vol. I. London: Henry Southern & Co. 1921. In two volumes. Price 3 Guineas net.

This remarkable work (the writer of the preface modestly calls it a catalogue), was commenced in 1906, and gradually assumed the proportion in which it now appears, occupying two well-bound volumes, and extending to 964 pages. The work is claimed to be the first historical catalogue of science that has been published; it is certainly the most complete that we have seen, and will undoubtedly be welcomed by all lovers of books. The illustrations, which form the striking feature of the work, are half-tone plates printed on special paper, and include besides facsimiles of illustrations and portraits, textual passages from the more important works; it is claimed that many of them are reproduced for the first time

The books are arranged in alphabetical order, together with the price, bibliographical particulars, and historical references.

The value of the work is still further enhanced by the inclusion of a very complete Index, which embraces not only the books in the catalogue, but also those of further lists that have been published since the "Chemico-Mathematica" was printed; this, although it lacks the interest due to the illustrations that are given in the main volume is in itself a valuable asset. The authors express their indebtedness to Heinrich Zeitlinger of Linz, "a well-wisher of learning and of England," to whom is due the greater part of the work.

J.H.G.

*Extra Pharmacopœia of Martindale and Westcott.* Revised by W. HARRISON MARTINDALE, Ph.D., F.C.S., and W. WYNN WESTCOTT, M B. (Lond). D.P.H. Seventeenth Edition. Vol. II. London: H. K. Lewis & Co, Ltd. 1921. Price 17s. 6d.

This volume forms an addition to Vol. I., which was issued in June, 1920. The authors state in their preface that they have submitted many of the statements that have appeared in recent scientific literature to laboratory test; the general results of these experiments are given in alphabetical order in the early pages of the book. These practical notes cannot fail to be of value. The section includes a short but comprehensive account of the science of Radiology Ultra-Violet Light. Of course, it is not intended to be other than a condensed note, but the condensation has been pushed to such a degree that we almost fear it may be misleading. In referring to the theory of Isotopes, we notice the bald statements that "Mercury is composed of five or six isotopes, Neon is a mixture of isotopic elements of different weights, as is also Chlorine." Should this meet the eye of a pharmaceutical student with but little knowledge of modern science, the result might be confusing.

The Bacteriocidal and Clinical notes are extremely good and valuable. The general contents and scope of the work are so well known that it is not necessary to go further; but enough has been said to make it clear that it has been brought quite up-to-date and contains its full value of information.

J.H.G.

*The Condensed Chemical Dictionary.* Compiled and Edited by the Editorial Staff of the Chemical Engineering Staff of the *Chemical Engineering Catalog* (F. M. TURNER, Jr., Technical Editor). Pp. 525. New York: The Chemical Catalog Co., Inc., 1, Madison Avenue.

This book gives a list of chemical substances in alphabetical order, giving their synonyms (if any), colour, and properties, constants, solubility, containers, uses, railroad, shipping regulations, &c.

This should prove a valuable help to not only the non-technical mind, but also to the chemist, who comes up against substances of which he wants a little knowledge, but being not directly concerned with it in his everyday routine of business, has generally to search through either one of the big dictionaries on chemistry or an academical treatise.

To give an example of the method employed in this book, one is taken at hazard:—

*Dioxyanthraquinone* (*Chrysazine*)

$C_{14}H_6O_2(OH)_2$ 1 : 8.

Colour and properties: Reddish-brown needles.
Constants: Melting-point 191° C. Soluble in alcohol; sparingly soluble in water.
Derivation: From dinitroanthraquinone (1 : 8) by reduction and subsequent diazotization.
Method of purification: Crystallisation.
Grades: Technical.
Containers: Wooden kegs.
Uses: Dyestuffs.
Fire hazard: None.
Railroad shipping regulations: None.

The dictionary is primarily compiled for the use of exporters and importers, brokers, lawyers, insurance companies, and many other classes of firms and individuals who have frequent need for information regarding chemicals and chemical products. Beside the dictionary proper there are a few pages relegated to the definition of units, also temperature conversion tables, &c. It should prove very useful to those for whom it is intended.

N.B.M.

*Elementary Practical Chemistry. Part I., General Chemistry.* By FRANK CLOWES, D.Sc. (Lond.), and J. BERNARD COLEMAN, A.R.C.Sc. Seventh Edition. Pp. xvi+241. London: J. & A. Churchill. 1920. Price 6s.

This little volume is especially intended for pupils of secondary schools, and other students who are not training for the profession of consulting and analytical chemistry. It accordingly comprises a course of instruction which gradually presents the principles of chemistry to the student by means of a selected series of experiments.

It commences with a description of the metric system of weights and measures, and the determination of density and temperature. Concise directions are then given for the preparation and use of some simple bench apparatus, such as the making of a wash-bottle, and the mounting of a platinum wire. The student next studies the composition of air and water, the process of combustion, and the properties of some important non-metals and metals and their compounds.

Many quantitative experiments are given, including some which illustrate the laws of chemical combination and of chemical equivalence, and the relation of acid to alkalis as regards their neutralising power.

The book is divided into fourteen sections, the last being comprised of miscellaneous exercises, such as the preparation of crystalline salts, &c. An Appendix is added in which is given a list of atomic weights, chemical equivalents of elements, conversion of tables of thermometer scales, and other data useful to the student.

N.B.M.

*A Text-book of Organic Chemistry.* By A. F. HOLLEMAN, Ph.D. Edited by A. JAMIESON WALKER. Fifth Edition. Pp. xviii.+642 1920. London: Chapman & Hall. Price 18s. 6d. net.

The first English edition of this text-book was published in 1903, and it has just appeared in its fifth edition, which shows how much the author's work has been appreciated. In the two parts the whole field of organic chemistry is well covered. The first part deals with the aliphatic compounds; the second with the cyclic compounds. There are illustrations occurring through the book to render the text more easily understood. The book has a good index, which runs into 32 pages.

N.B.M.

*Laboratory Manual of Organic Chemistry.* By HARRY L. FISHER, Ph.D. Pp. x+331. London: Chapman & Hall, Ltd. 1920. Price 12s. 6d. net.

The book is divided into two parts: Part I., headed "Laboratory Experiments," gives a series of experiments both on the detection of organic radicles and the preparation of organic compounds. This part includes 66 experiments, and the author has marked the most important of them with an asterisk; that is to say, students who are not taking chemistry as a profession but must have a general groundwork in the subject, such as medical students, would only tackle those so marked.

Part II., entitled "Organic Combustions,' deals with the quantitative analysis of organic radicles; division A dealing with the determination of carbon and hydrogen; division B with nitrogen.

N.B.M.

*Die Schwimmanfbereitung der Erze.* By Dr. PAUL VAGELER. Dresden and Leipzig: Theodor Steinkopf. Price 4s. 4d.

The use of flotation methods for the concentration of ores has been greatly extended recently, and is now widely employed in various parts of the world, and for many different kinds of ores. More than 70 million tons of ore are now treated by flotation processes annually, and there is every reason to believe that this does not represent by any means the maximum amount that can be reached, although it does not appear at all probable that wet methods will ever be entirely superseded. This book, which is a short *resumé* of the work that has been done upon the theory and practice of these processes, comes at an opportune moment, and will be found to give a useful outline of the subject. The factors to be taken into account in applying the method are reviewed shortly, and such questions as the choice of oils are well discussed and summarised. The author is inclined to claim too much for German skill and enterprise, and the references to English and American literature are distinctly inadequate, while the lists of potent specifications include only those taken out in Germany. Hence there are many omissions of very important patents which considerably reduces the value of the book. The author attributes most of the advances that have been made to the work of German chemists, and evidently considers that the methods of "patent trial" adopted by the scientific men of other nations are hardly to be regarded as true research work. However, the book has a real value as a careful compilation and summary, and in many cases it indicates the directions in which useful research work is waiting to be done.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. clxxii., No. 23.

"On Titanium Peroxide."—By M. Maurice Billy.

"Contribution to the Study of Oils derived from Grape Pips."—By M. Emile André.

"On Some New Sulphonate Derivatives of Oxindol and Isatin —By MM. J. Martinet and O. Dornier.

"Allotropic Modifications of Oxides."—By Mdlle. S. Veil.

"Preparation of Mixed Secondary and Tertiary Phenolic Amines."—By M. A. Mailhe and F. de Godou.

No. 24.

"Surface-tension of Mercury in Different Gases."—By M. Jean Popesco.

"Molybdo-malates of Ammonium and Sodium." By M. E. Darmois.

"Action of Sodium Carbonate on Chrome Alum Solutions."—By MM. L. Meunier and P. Caste.

"Dehydration of Phenyl-1-dimethyl-2·2-butanol-1, and Diphenyl 1-3 dimethyl-2·2-propanol-1."—By Mdlle. Jeanne Apolit.

"Composition of the Essence of French Turpentine, and of the Bromide of $\alpha$-Pinene."—By M. Pauselle.

"The Tetrahydronaphtols." — By MM. A. Brochet and R. Cornubert.

"Influence of Ammonium Molybdate on the

Rotatory Value of Mannite."—By M. Georges Tauret.

"Decomposition of Metallic Alcoholates and Phenates by Heat."—By M. J. F. Durand.

"Stereoscopic Photography of Crystals."—By M. Maurice François.

"Some Crystalline Rocks of Albania."—By MM. Jacques Bourcart and René Abrard.

## NOTES.

Unladen Weight of Heavy Motorcars.—The General Secretary of the Commercial Motor Users' Association (Inc.) draws attention to the importance of seeing that the unladen weight which is painted on the offside of every heavy motorcar corresponds with the unladen weight as shown on the licence. Proceedings were recently taken by the police in the City of London where the weights shown on the licences were 7¼ tons and the weights on the vehicles were 5 tons, being the old registered weights. In a number of cases these proceedings were withdrawn, owing to the intervention of the Ministry of Transport at the instance of the Association. The Heavy Motorcar Order, 1904, has now been amended by increasing the maximum unladen weight of heavy motorcars to 7¼ tons, and the maximum combined unladen weight of a heavy motorcar and trailer to 9¾ tons. Users of heavy motor vehicles who desire further information are recommended to communicate with Mr. F. G Bristow, General Secretary, Commercial Motor Users' Association (Inc.), 50, Pall Mall, London, S W. 1.

British Engineers' Association. — Although the British Engineers' Association, being a purely trade association, confines its activities to the promotion of the commercial interests of the engineering industry, and plays no part in labour disputes or wages negotiations, it is vitally interested in their effects upon output, costs of production, and selling prices. As representing the commercial side of the industry, *i.e.*, the side concerned with the profitable disposal of the products of their joint labours it may claim to speak alike in the interests of employer and employed. The present situation in the engineering trades is so grave, and the consequences to the nation threaten to be so serious, that the Council feel it their duty to present the following facts and reflections for the earnest consideration of all engaged in the engineering industry, both masters and men, and of every thinking citizen. Even before the national stoppage of work in the coal mines, a critical situation was rapidly developing in the engineering industry, because our costs of production were far too high in relation to the purchasing power of an impoverished world, in which many prospective customer countries were further restrained from buying by adverse exchanges, entailing insupportable losses. A contributory cause of our loss of trade was the ability of the United States, Germany, and Belgium to undersell us. To the extent that Germany has been able to produce and export the depreciation of her exchange has enabled her to quote prices with which the British engineering manufacturer could not possibly compete. In a lesser degree this also applies to Belgium. In spite of the strenuous efforts of directors and managers, of which we have abundant evidence, our engineering firms are quite unable to secure the volume of business required to replace the orders executed during the last six months, or now rapidly approaching completion. The fact is that although the world is in urgent need of vast supplies of products of engineering industry, to make good the losses due to the war and increase the future rate of wealth production, these supplies cannot be ordered until prices are brought within the purchasing power of the customer. This applies even to the home market, where many big schemes are being held in a state of suspense because of the prohibitive cost of carrying them into execution at present prices. To the extent that our competitors can undersell us, they will not only capture the overseas trade, but also invade our defenceless home market. It must not be imagined that the resumption of coal-mining will, by itself, revitalise the engineering industry, even though the settlement be on terms consistent with a low enough price for industrial coal. It cannot be too clearly and widely understood that the engineering industry has no chance of recovery unless and until a substantial reduction has been made in the costs of production. This is the problem to be solved, and failing its solution, other considerations will be of little more than academic interest. At some time, in the not very distant future, masters and men in the engineering trades will be compelled by the pressure of stern necessity to compose their differences and agree upon a *modus vivendi*. All their thoughts and energies will be needed for the task of salving the industry by which they live. Delay in making this great constructive effort will merely increase the amount of leeway to be painfully and laboriously recovered, and imperil the chances of ultimate success.—D. A. Bremner, Director.

Reactions of Carbon Monoxide and Iron Oxides.—Moissan demonstrated that when CO reduces ferric oxide, $Fe_3O_4$, FeO, and finally Fe are successively produced. The two last reactions are limited by oxidation of iron and ferrous oxide due to carbonic anhydride. M G. Chaudron resumed these experiments, utilising a device enabling the employment of the interferential method for analysis of the gaseous mixture. The three solid phases coexist in equilibrium at 580° C., and at a lower temperature the ferrous oxide gives a magnetic mixture of iron and oxide. This last transformation is reversible.—*La Nature*, March 19, 1921.

The Non-Toxicity of Copper Salts for Mildew.—Since 1886, subsequently to the work of Millardet, the employment of copper salts seemed to be essential in the composition of anti-cryptogamic mixtures. M. and Mme. Villedieu have already contradicted certain hypotheses hitherto accepted, regarding the formation of a hydrocarbonate which, dissolving in rain water, would give a medium where life of zoospores would be impossible. The new note demonstrates that the conidia of mildew develop, and then, in

turn, germinate in a cupric solution. The action of the mixtures hitherto employed is not then in any way due to the metal, suppression of which is to be considered in the composition of anticryptogamic mixtures.—*Comptes Rendus*, Feb. 7, 1921.

A NEW organisation, under the title of The Federation of British Propaganda Societies has been formed, the object of which is to co-ordinate the work of propaganda societies and, as far as possible, prevent overlapping. Already about 15 propaganda societies have expressed their willingness to join. His Grace The Duke of Northumberland has consented to act as President, and Sir Henry Birchenough, K.G M.G., is the Treasurer. The General Secretary is Mr. David Gilmour, O.B.E., Sicilian House, Southampton Row, London, who will be willing to give further information to any of our readers.

OUTPUT OF BROMINE IN U.S.A. IN 1920.—The New York *Journal of Commerce* states that bromine, which is derived from brines pumped from deep wells in Michigan, Ohio, and West Virginia, was produced by eight firms in the United States in 1920. The output, according to the United States Geological Survey, Department of the Interior, was 1,160,584lb., valued at $745,381, a decrease of 37 per cent in quantity, and nearly 40 per cent in value from the output of 1919 The quantity produced, however, was greater than in any year before 1918. The average price per pound received by the producers rose from 13 cents in 1910 to $1·31 in 1916, and was 64 cents in 1920, which is more than three times the average price in the year before the war. The New York quotations on bulk bromine, which ranged from 70 to 90 cents in the summer of 1920, were 50 to 52 cents in December, and are now about 40 cents.—*Department of Overseas Trade.*

AN INDUSTRIAL OPTIMIST.—Mr. H. G. Williams, M.Sc., a member of the Industrial League and Council seems to be an optimist of the first water Months ago he was predicting what at the time seemed an impossible fall in the cost of living, but events have substantiated his assertion, and now he is equally emphatic on the point of a trade revival. With the nation still in the throes of countless industrial differences, on the verge of maturing to formidable dimensions, one must, indeed, be sound of heart to acquiesce with him in his optimism. Yet, so accurate has Mr. Williams been in his prognostications heretofore, that he may infuse a degree of confidence where pessimism prevails. It was towards the close of January this year that he wrote: "By May, retail prices should be about a fifth lower than they were on November 1st, 1920, and the cost of living should then be about 120 per cent above pre-war level. I venture to predict that by the end of the summer the level will have fallen to about double pre-war prices, *i.e.*, 100 per cent." Were it not for the coal dispute, there is not the slightest doubt that the index figures for the cost of living published on May 1 would have been well below the prophetic figure of 120 cited by Mr. Williams, instead of standing at 128. How near he will prove to be accurate in his contention that the cost of living will be down to 100 per cent by the close of the summer remains to be seen. In the current issue of the *Industrial League Journal* he says: "The world-wide indications at the moment show the beginning of a general revival of commercial confidence. A world revival in trade may be predicted with considerable certainty, and this country will share in that revival provided that British goods can be offered at prices sufficiently attractive. This will probably involve employers and employed making adjustments in their minds as to the money value of the profits and wages which they can reasonably expect to obtain, but even more important is the increase in individual production which will ensure lower selling prices without the necessity of any serious lowering of the standard of living, though, temporarily, both employers and employed may find themselves forced to accept a lower standard than they have enjoyed in the recent past." Mr. Williams has on more than one occasion voiced the opinion that it will not be long ere the cost of living will be down to 75 per cent above the pre-war figure. It seems like anticipating the millenium.

THE POLISH POTASH INDUSTRY.—It is quite probable, when the frontiers of New Poland are definitely fixed, that the districts of Steppenitz and Kalusz, comprising deposits of salt and potash, in East Galicia, will be allotted to this country. Hitherto potash has only been mined at Kalusz, the deposit being industrially workable, in the opinion of experts. The Kalusz deposits contain chlorides and sulphates of potassium and magnesium, and the upper bed sylvinite and kainite. The bed of kainite is 10 to 12 metres thick, and in some places 17. There are four distinct beds of potash. The sylvinite bed is about two metres thick, and contains 25 to 60 per cent of potassium chloride. The second bed is 1·5 metres thick, and has 12 per cent potassium chloride, being situated 30 metres below the kainite deposit. Below the chief deposit there is a third sylvinite deposit, consisting of two beds, containing 42 per cent potassium chloride, 12 to 80 metres thick It is not very probable that the potash mines of East Galicia will be of great importance to foreign markets, and the Kalusz mines can only be of local importance.—*Chimie et Industrie*, May, 1921.

## NEW COMPANIES.

The under-mentioned particulars of New Companies recently registered are taken from the Daily Register compiled by JORDAN & SONS, LIMITED, Company Registration Agents, Chancery Lane, W.C.2.

CLIMAX MANUFACTURING COMPANY, LIMITED.—(175211)—Registered 15th June, 1921. 283, Victoria Dock Road, West Ham, Essex. To carry on the business of Chemists and Druggists. Nominal Capital: £1,200 in 1,200 Shares of £1 each. Directors: A. Curtis, Groveley, Feltham Hill, Middlesex; D. Cable, 5, Avondale Road, Mottingham, Kent; S. J. Coxwell, Milton Lodge, First Avenue, Westcliff-on-Sea. Qualification of Directors: £100. Remuneration of Directors. To be voted by Company.

KLEANEESE SOAP COMPANY, LIMITED.—(175219)—Registered 15th June, 1921. 47, Church Street, Stoke Newington, N.16. To acquire and carry on the business of Soap and Polish Manufacturers. Nominal Capital: £500 in 1,000 Shares of 10/- each. Directors: P. H. Bateman, 23, Vesta Road, Brockley, S.E.24.; G. Hartrodt, 120, Greenwood Road, Hackney, E.8.; D. Bailey, Beechwood, Moss Lane, Pinner. Qualification of Directors: 1 Share. Remuneration of Directors. To be voted by Company.

## New Patents.

This List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W.C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

15732—Badische Anilin & Soda Fabrik —Production of oxalic acid June 7.
15815—Chemical & Metallurgical Corporation, Ltd.—Treatment of argentiferous lead-zinc-sulphide ores. June 8.
16148—Craig, E. N.—Electrolytic treatment of metalliferous materials containing tungsten or molybdenum. June 11.
15931—Dreyfus, H.—Treatment of products of cellulose derivatives. June 9.
16159—Liebreich, E.—Process for separating-out metallic chromium. June 11.

*Specification published this Week.*

164034—Cocking, A. T. and Lilly, C. H.—Production of glycerine by fermentation.

*Abstract Published this Week.*

*Treating Lead-Zinc Ores.*—Mr. E. F. Elmore of Boxmoor, Hertfordshire, has obtained a Patent No. 162026 for a process of treating argentiferous lead-zinc sulphide ores. They are roasted with a halogen salt such as sodium, potassium, calcium, or magnesium chloride in an oxidizing atmosphere at a temperature above 400°C. but not high enough to volatilize lead chloride, but zinc sulphide remaining for the most part unattacked. To prevent any appreciable attack on the zinc the temperature should not exceed 500°C. The air employed in the roasting is preferably moistened if dry. The product of the roasting is leached with hot brine to extract lead, some silver and any zinc chloride. The lead and silver are recovered in any known manner, for instance, by cooling the solution and treating the deposited chlorides as described in Specification 129773 to separate the silver as argentiferous lead sulphate, the brine being used repeatedly. The residual ore is treated with a solvent for silver such as a solution containing 35 per cent calcium chloride and 3-5 per cent cupric chloride or 3 per cent hydrochloric acid as described in Specification 151698 or, if there is an appreciable quantity of lead, the ore is first treated with hot brine containing hydrochloric or sulphuric acid as described in Specification 127641 to extract the lead and part of the remaining silver, and then as above described to extract the remaining silver. The used brine containing sodium sulphate and the lead salts obtained may be treated as described in Specification 129773 to de-sulphate the brine and obtain lead sulphate. In a modification if there is some unoxidized lead sulphide remaining after the roasting or after the leaching with brine, the ore is leached with hot strong solution of calcium or magnesium chloride containing enough hydrochloric acid to convert the lead sulphide into chloride. This effects a good extraction of the silver and renders a subsequent extraction unnecessary. If it is preferred to have a small quantity of zinc chloride present in the calcination, which may be derived from the ore if it contains some easily attackable zinc, or, may be added at the beginning or towards the end of the calcination, preferably as a mixture of sodium and zinc chlorides obtained by evaporating some of the brine used for leachings Specifications 131353, 135968 and 141044 also are referred to.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.



## NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemical Apparatus, &c., for review or notice to be addressed to the Editor.

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THE CHEMICAL NEWS.
VOL. CXXIII., No. 3195.

## WHITLEYISM THE ONLY SOLUTION.

### CONSIDERED VIEWS OF THE INDUSTRIAL LEAGUE AND COUNCIL.

WE have received the following memorandum from the Industrial League and Council:

The extremely critical position into which Industry has now drifted gives cause for the gravest anxiety. Disputes of a national and local character have created a feeling of instability to all concerned. Confidence, the bed-rock of trade and commerce, must be restored to the world. Industry is almost at a standstill, and our foreign trade, both imports and exports, shows an alarming decrease. The Industrial League and Council have given this matter very serious consideration, and are convinced that no permanent or substantial change will occur until there exists a greater confidence between employers and employed. The development of Labour and Employer organisations on antagonistic lines places the two bodies in opposing camps from which they tend to view each other with hostility. From circumstances such as these it is hardly possible for anything to accrue but disputes, strikes, and lock-outs.

The formation of a National Joint Industrial Council would not, in the opinion of the Industrial League and Council, do much to lessen the tension existing. Rather would it add to the difficulties, as a National Joint Industrial Council, whilst it would be useful for the exchange of opinons, would be too unwieldy and complex to be of any use as a means for industrial harmony. As an alternative, the Industrial League and Council advocates strongly the formation of Joint Industrial Councils in every industry as the only means whereby disruption in industry may be avoided; 70 of these have already been established, most of which have been very successful.

The world is suffering from a complete shortage of almost, if not all, the necessaries of life, and only years of hard work and sacrifice on the part of all, whether employers or empolyed, will in any way remedy the circumstances. The warlike policy which still unhappily characterises our industrial relations can lead to nothing but disaster for the whole community. Lost foreign markets are extremely difficult to re-establish, and lost time caused by industrial disputes is an important factor in maintaining high prices. The recent mining dispute has lost to the miners at least £55,000,000 in wages; it has lost to Industry countless millions of pounds sterling. Joint Councils of Employers and Employed in the mining, as in other industries, would, in the opinion of the Industrial League and Council, minimise the possibility of disputes, and would bring harmony and prosperity to the industry. The total number of workpeople involved in disputes during the last 12 months is 5,414,000, and the total working time lost is 72,885,000 working days; these are independent of the vast body of workers who were otherwise out of employment, of whom no less than nearly 8 millions drew unemployed pay during the same period. Time and labour lost is a reduction in national wealth and affects every member of the community.

The Industrial League has from its inception in 1915 resolutely abstained from any interference in trade disputes. It has consistently advocated the better relations a s between employer and employed, and has since 1917 assisted in establishing Whitley Councils. It is strongly of opinion that the time has arrived when every industry, no matter how well organised it may be on either side, should have its Joint Industrial Council.

Amongst the signatories to the memorandum are the following members of the Executive Committee of the Industrial League and Council: Viscount Burnham, C.H., Rt. Hon. G. H. Roberts, M.P., Sir Wm. Peake Mason, Bart., Mr. John Baker (Iron and Steel Trades Confed.), Mr. E. J. P. Benn, C.B.E., Mr. A. Bellamy (Ex-President N U.R.), Mr. Hugo Hirst (General Electric Co.), Mr. E. W. Petter (Messrs. Vickers Petter, Ltd.), Mr. Robt. Young, M.P.

Events of the past week strikingly illustrate the fact that if anything will bring this country back to a state of productivity and place our industries in a position to successfully compete in all the markets of the world, it is the practical appreciation of the principles of Whitleyism. In this respect facts substantiate the views expressed by the Industrial League and Council.

For instance, in the wool textile industry, peace for at least a year has been accomplished by the satisfactory manner in which the National Wool (Allied) Textile Industrial Council on Monday the 27th ult., came to agreement on a different wage question.

A similar report comes to hand in respect of the flour milling industry, the operation of which directly effects every person in the land. On Wednesday, the 29th ult., a wage cut of 7s. 6d. per week was agreed upon by the National Joint Industrial Council for this industry.

The railways have embraced Whitleyism; the printers, by reason of its operations have been without serious strife for a long period, and are at this moment amicably discussing a proposed wage reduction. Farm workers are anxious to obtain a Whitley Council because they appreciate its value, and this week also, the dockers are discussing at the Board of their National Joint Council for the Docks the all-absorbing wage question, and will, no doubt, arrive at a solution of their difficulties without strife. These are but few of the happenings in the world of Whitleyism tending to shape the future welfare of our people. These Councils have been working steadily and unobtrusively for months past, and it is only on rare occasions they figure in the limelight, and then only because all sections engaged in an industry are unable to see eye and eye on a particular matter.

## SOIL ACIDITY IN ITS PHYSICO-CHEMICAL ASPECTS.*

By E. M. CROWTHER, Rothamsted Experimental Station.

THE application of basic materials, such as lime or chalk, has long been known to result in increased soil fertility, especially in the case of the so-called "sour soils." Such soils are recognised in practice by a fairly characteristic weed flora,

*A Contribution to a General Discussion on "Physico-Chemical Problems Relating to the Soil" held by The Faraday Society, on Tuesday, May 31, 1921.

the failure of leguminous crops, and the liability of cruciferous crops to certain fungoid diseases. Sour soils redden blue litmus paper when it is pressed on to the moist soil, so that the obvious view was avanced that the infertility is due to the presence of acids, which are neutralised by the application of lime. Methods for the determination of the amount of this acidity and therefore of the "lime requirement" of the soil, were devised on the assumption that the interaction between a sour soil and a base was a simple neutralisation. (Examples of such methods are the Veitch method involving the addition of lime water in slight excess, and the Hutchinson-McLennan method in which the $CoCO_3$ removed from a calcium bicarbonate solution is estimated).

A second group of methods depended on the curious fact that sour soils set free considerable amounts of titratable acid from salt solutions such as KCl or $KC_2H_3O_2$.

A large amount of work has been devoted to the investigation of the validity of these lime requirement methods. Several of them have provided quite useful practical information, but their application is circumscribed by the fact that it is only on comparable soils that the "lime requirements" adequately represent the response to limeing. Further, all the methods are very sensitive to slight variation in technique, and different methods give widely divergent results when applied to the same soil. In a recent study of the Hutchinson-McLennan method, Fisher has shown that the amount of $CaCO_3$ removed from solution is not independent of the concentration of the bicarbonate used, but that the distribution of $CaCO_3$ beween soil and solution may be represented by the usual adsorption equation. The taking-up of base by a sour soil appears to involve not only the simple neutralisation of acids, but also some absorptive process by the soil colloids.

Many workers have attached more importance to the absorption than to the presence of acids. It has been held that in fertile soils, well provided with reserves of $CaCO_3$, the absorptive power of the soil colloids for bases is fully satisfied, but that the continuous removal of the basic material by plant growth and drainage may result ultimately in a colloidal system with a marked affinity for bases. Ramann therefore replaced the term "acid" as applied to soils by "adsorptively unsaturated." Baumann and Sully, working with peat soils, and Cameron and Harris with mineral soils, denied the existence of acids in soils giving aqueous neutral to litmus paper. Selective adsorption of bases was held to account not only for the action of litmus paper and for the liberation of acid from salt solutions, but for the large variations in the amounts of different bases taken up by the soil from alkaline or neutral solutions. The possibility of establishing the existence of acids in the soil by titration was the subject of prolonged controversy. Truog, for example, maintained that by using diluted solutions to reduce side-reactions, equivalent amounts of NaOH, $Ca(OH)_2$, and $Ba(OH)_2$ were neutralised by sour soils.

### *The Measurement of the H·-Concentration of Soils.*

The lime requirement methods were intended to measure the "quantity factor" of acidity, *i.e.,* the total amount of acid as measured by titration. But the acid properties of a solution can only be expressed by the "intensity factor," *i.e.,* the hydrogen ion concentration (or activity). Many sour soils have been shown to possess a H·-concentration considerably greater than that of water, so that there is now no valid reason for denying the existence of acid substances in sour soils.

The use of the hydrogen electrode is practicable in complex mixtures only if they possess considerable buffer action, *i.e.,* some mechanism for maintaining an almost unchanged reaction on the addition of small quantities of acid or alkali. Aqueous extracts of soils are but feebly buffered; the introduction of a little alkali, such as the ammonia produced by the reduction of nitrates by the hydrogen electrode, causes considerable alteration in reaction. Suspensions of soil in water, however, are strongly buffered, and give quite definite results with the hydrogen electrode. A very wide range of H·-concentrations has been recorded; thus Gillespie found values for $-\log [H^\cdot]$ or pH from 4·4 to 8·6. Sharp and Hoagland with a somewhat less satisfactory technique found a range of 3·7 to 9·3, though the fertile soils examined by them showed very similar values, varying from the neutral point to about 7·5 on the alkaline side.

The potential difference which forms the basis of the method can be measured with a high degree of accuracy, but with soils difficulties are introduced by the necessity of working with suspensions. Measurements cannot be made on soils at their natural water or $CO_2$ contents. In well-buffered mixtures, dilution produces little alteration in reaction, and it has been found that variation in the soil-water ratios or the addition of moderate quantities of $CO_2$ to the hydrogen used, produces but little alteration in the results obtained. It is therefore generally assumed that the values obtained aproximate to those of the soil solution.

The sulphone phthalein indicators of Clark and Luhs have been used for the determination of the H·-concentration of aqueous soil extracts, and, in the only comparison hitherto made with the results for soil suspensions by the hydrogen electrode, Gillespie has obtained very satisfactory agreement. This is especially important because the most probable sources of error in the two methods arise from different causes. The principal difficulty involved is the preparation of sufficiently clear soil extracts for colour matching. Prolonged centrifuging is often insufficient and it is then necessary to resort to dilution, since filtration or flocculation often produces quite marked changes in such weakly buffered solutions.

Considerable importance has been attached in the past to the differences towards litmus paper exhibited by the moist soil and the soil extract. An insensitive indicator such as litmus, especially on paper, requires an appreciable amount of acid to effect the change to red. With small quantities of weakly buffered solutions, such as soil extracts or very dilute HCl, the reaction of the liquid may be seriously changed, whilst if a large bulk of solution be left in contact with the litmus, leaching may occur before the correct tint is reached. When the paper is pressed on to the moist soil, the proximity of the soil allows rapid diffusion of acid to the paper, whilst its reaction is changing, and a fair indication of the soil reaction may be obtained.

The mechanism of buffer action in the case of partially neutralised weak acids is easily explained in terms of the dissonation constant, but it is not generally possible to analyse the factors involved in more complex systems. The difficulties of technique have prevented much work on the determination of the changes in $-\log [H^{\cdot}]$ during the titration of acid soils with bases, but it has been found that the soils are well-buffered over considerable ranges of $H^{\cdot}$-concentration. In other words, the titration curves showing $-\log [H^{\cdot}]$ as a function of the amount of base added are practically linear without any sharp breaks corresponding to "end points." The slopes of the curves vary considerably from soil to soil, so that it is possible for a strongly acid soil to possess little titratable acidity or a low lime requirement, whilst neutral or even slightly alkaline soils may show an appreciable requirement if the soil be brought into equilibrium with an alkaline solution.

*Action of Neutral Salts on Acid Soils.*

Sharp and Hoagland have shown that $BaCl_2$, KCl, or NaCl increase the $H^{\cdot}$-concentration of suspensions of acid soils. In a more detailed study of the action of salts on humus suspensions Gillespie found that the same action occurs and that the increases produced by different chlorides are in the order Ba>Na>K. The interpretation of these results is complicated by the fact that these salts produce similar, though smaller, increases in the $H^{\cdot}$-concentration (or activity) of true solutions.

The increase in $H^{\cdot}$-concentration is accompanied by considerable amounts of titratable acid, the estimation of which was used in some of the early lime requirement methods. In spite of much investigation, the interpretation of this action is still obscure. On the selective adsorption theory the action is regarded as strictly analogous to the liberation of acid and fixing of base during the precipitation of colloidal solutions of $As_2S_3$ by $BaCl_2$. The importance attached to the adsorption of cations for the coagulation of negative colloids gave some support to this view, but no clear mechanism was advanced to explain the liberation of acid.

Neutral salt extracts of acid soils contain weak bases—chiefly Al, though Fe, Mn or even Zn are sometimes found—in amounts roughly equivalent to the titratable acidity. Parker modified the selective adsorption view by assuming that the salt is hydrolysed, the base being adsorbed whilst the acid dissolves the weak bases from the soil. Others regard the aluminium salts as the cause rather than the result of the acidity of the neutral salt extracts. Rice found that the relations between the $H^{\cdot}$-concentration and titratable acid of $KNO_3$ extracts corresponded closely with those of mixtures of $Al(NO_3)_3$ and $KNO_3$, and concluded that the amount of aluminium was precisely equivalent to the titratable acid, the apparent exceptions arising from the difficulties of analysis and titration. Rice and Daikuhara regard this basic exchange as taking place with loose adsorption compounds of weak bases which characterise acid soils, whilst Veitch and later workers hold that the interaction occurs with the complex alumina-silicates of the soil. Whatever the mechanism of this basic exchange, the differences in the hydrolysis and solubilities of the various salts concerned will account for many of the results. The excess of a salt of a weak acid prevents any considerable rise in $H^{\cdot}$-concentration, so that the aluminium salts are almost completely hydrolysed and precipitated with the liberation of much-titratable acid, whilst with salts of strong acids higher $H^{\cdot}$-concentrations occur, so that the Al remains in solution and the reaction soon reaches an equilibrium point. Similar reactions of the aluminates and silicates of Ca or K will account for the greater adsorption of Ca during the action of the hydroxides on sour soils. In the case of peat soils Sven Odén suggests that the acidity of salt extracts arises from the displacement of small amounts of organic acids adsorbed by humus. He found no HCl by distillation of a KCl extract of an acid peat, and an aqueous extract of the treated peat was not alkaline, so that there was no evidence of any hydrolytic decomposition by adsorption.

The complexity of the soil system is such that nothing is to be gained at present by formulating any general theory of the origin and nature of soil acidity.

*Relation of Soil Acidity to Plant Growth.*

Until recently soil acidity has been regarded as a pathological condition to be avoided by liming, but the reaction of the soil may vary within fairly wide limits and it does not follow that $-\log (H^{\cdot})=7{\cdot}07$ is the optimum for plant growth. Soil fertility is the resultant of the interaction of a large number of factors on the plant, and these factors are likely to be influenced to different degrees by the reaction of the soil solution. There is evidence that a distinctly acid reaction may be desirable for certain crops, and attempts are being made in New Jersey to increase the acidity of potato soils by the production of $H_2SO_4$ through the oxidation of sulphur added to the soil.

The reaction of acid soils is frequently of the same order as that of plant roots, so that the infertility of most acid soils would not appear to be due to the direct action of the acid on the roots. Of the indirect effects Truog attaches the greatest importance to the lack of available basic material, such as $CaCO_3$, for the neutralisation of the acids produced in the plant, whilst several workers have ascribed the infertility to the toxic action of aluminium compounds. Gillespie has recently made some preliminary measurements of the reduction potentials of water-logged soils, and has suggested that the "sourness" of poorly drained soils may be the result of their high reducing power.

An extensive bibliography of soil acidity is given by E. A. Fisher, *Journal of Agric. Science*, 1921, xi., 19.

## THE CLINTON WATER SUPPLY AND THE MISSISSIPPI RIVER.

By RUSSELL MORGAN.

THE water supply of Clinton, Iowa, situated on the Mississippi River, comes from a series of five wells located above the city. The wells are 200ft. to 250ft. from the river, and from 1800ft. to 2200ft. in depth. The numbers here given express the amounts of the various substances in a million parts of the water.

| | |
|---|---|
| Total solid residue | 251·8 |
| $SiO_2$ | 1·0 |
| $Fe_2O_3$ and $Al_2O_3$ | 1·60 |
| $CaCO_3$ | 54·60 |
| $CaSO_4$ | 52·10 |
| $MgCO_3$ | 27·40 |
| NaCl and KCl | 116·00 |
| Phosphates | 0·0 |
| Nitrite nitrogen | 0·0 |
| Nitrate nitrogen | 0·1 |
| Free ammonia | 0·015 |
| Albuminoid ammonia | 0·06 |

*The Water from the Mississippi.*—The sample was taken from about the middle of the stream. The water was slightly cloudy, so we filtered it through a paper.

| | |
|---|---|
| Total solid residue | 219·2 |
| $SiO_2$ | 13·8 |
| $Fe_2O_3$ and $Al_2O_3$ | 2·0 |
| $CaCO_3$ | 66·40 |
| $MgCO_3$ | 48·90 |
| $CaSO_4$ | 17·50 |
| NaCl and KCl | 69·80 |
| Nitrate nitrogen | 1·10 |
| Nitrite nitrogen | 0·008 |
| Carbon dioxide | 93·00 |
| Free ammonia | 0·04 |
| Albuminoid ammonia | 0·48 |

*The Unfiltered Water from the River.*

| | |
|---|---|
| Total residue | 259·0 |
| $SiO_2$ | 33·20 |
| $Fe_2O_3$ and $Al_2O_3$ | 2·6 |
| $CaCO_3$ | 94·10 |
| $CaSO_4$ | 17·50 |
| $MgCO_3$ | 48·60 |
| NaCl and KCl | 69·80 |

The cloudiness of the unfiltered river water seems to be due to a small quantity of silica and calcium carbonate in suspension.

The river water and well water contain a relatively large amount of chlorides, and the waters in most other respects are quite similar. Both are rather soft waters for this section of the country, where there is an abundance of dolomite rock. Although the wells are encased, there is a possible connection between the river and the wells.

Cornell College, Mount Vernon, Iowa.
June 4, 1921.

## AN EXTRAORDINARY NUMERICAL RELATIONSHIP BETWEEN CALCIUM AND STRONTIUM.

By ALEXANDER SAKOSCHANSKY, B.Sc.

It has been frequently stated that atomic weight numbers are something more than relative numbers. While with the present system numerical relationship of a simple type exists only with a few elements, such as $\sqrt{2{\cdot}43}=15588$, $23^2=529$, $3912^2=1529$, a system based on other numbers would place other elements in a numerical relationship.

The following is of particular interest, because the values have been derived in a systematic manner. If 0·11063 ($\log_{10}$ 1·290) be used as a multiplicand for atomic weights, it will give several pairs of corresponding values, *e.g.*,

Selenium × 11063 = Strontium
Sulphur × 11063 = Chlorine.

There are no other multiplicands which are as effective. Another way of expressing this relationship is $\frac{35{\cdot}46}{25{\cdot}46}\times 2{\cdot}30258=3{\cdot}207$, since 0·2546 is $\log_e$ 1·290, and 2·30258 is the conversion factor from $e$ to 10. (Note.—By analogy:—

$$Zn=\frac{65{\cdot}394}{55{\cdot}394}\times k=2{\cdot}7183;\ Mg=\frac{24{\cdot}32}{14{\cdot}32}\times k=3{\cdot}913).$$

Obtaining a system of atomic weights, chlorine = 25·46, Ca = 28·784, Sr = 62·918 (H = 0·7180).

$$(1)\qquad \frac{28{\cdot}784}{18{\cdot}784}\times k=3{\cdot}5284$$

$$(2)\qquad \frac{62{\cdot}918}{52{\cdot}918}\times k=\underline{2{\cdot}7377}$$

Now $\log_{10}\underline{1{\cdot}8784}=0{\cdot}27379$

and $\frac{\underline{\log_{10}3{\cdot}5284}=\underline{0{\cdot}27379}}{2}$

or $\sqrt[2]{3{\cdot}5284}=\underline{1{\cdot}8784}$

Barium shows an interesting numerical relationship which cannot be described in this short article.

In addition it should be noted that on the basis Cl = 25·46, fluorine and iodine are in logarithmic decrement, for F = 13·64, I = 91·12, $10\times 1/F=\log_x I$, $x$ = anti-$\log_{10}$ 1·365 = 1·352. Magnesium = 17·46.

## A STUDY OF ARSENICAL COMPOUNDS RELATED TO ARSPHENAMINE.

By GEORGE W. RAIZISS and JOSEPH L. GAVRON.

*Introduction.*

Experiences of the last decade have shown to the leading syphilologists that arsphenamine, which is the official American name for 3,3′-diamino-4,4′-dihydroxy-arsenobenzene dihydrochloride (P. Ehrlich and A. Bertheim, *Ber.*, 1912, xlv., 756), is one of the most efficient remedies in the treatment of syphilis. It has been observed by many that intravenous injections of this drug sometimes produce alarming symptoms. While these have been attributed to various causes, some relating to the condition of the patient, and others relating to he technic of adminisration, it seemed very probable to us that chemical impurities in arsphenamine may produce the disturbing effects Therefore, we deemed it advisable to prepare a number of compounds, which are closely allied to arsphenamine and which might appear as impurities in the drug in the course of manufacture.

Arsphenamine is produced by the reduction of 3-nitro-4-hydroxy-phenylarsinic acid which sometimes contains the corresponding dinitro derivative as an impurity. It is possible, therefore, that arsphenamine may be contaminated with 3,5,3′,5′-tetra-amino-4,4′-dihydroxy-arseno-benzene tetrahydrochloride. In view of this fact, it was of interest to prepare the latter compound and study its chemical and biological properties (J. F. Schamberg, G. W. Raiziss, J. A. Kolmer, and J. L. Gavron: "The Chemotherapy of Arsenical Compounds Related to Arsphenamine" (to be published

later). We observed also that it exerts a curative influence upon trypanosome infections, hence the preparation and study of derivatives of the above tetra-amino compound suggested themselves.

In the course of this work it was observed that an increase in the number of amino groups decreases the stabilty of both the phenylarsinic acids and the arsenobenzenes. On the other hand, the solubilities of the corresponding hydrochlorides in water are increased.

3,5-*Diamino-4-hydroxy-phenylarsinic Acid.*—This compound has been very briefly mentioned in a German patent (*D. R. P.*, 224,953, 1910), in which the method of preparation consists of the reduction of 3,5-dinitro-4-hydroxy-phenyl-arsinic acid by means of sodium hydrosulphite. The same compound has been prepared by us according to the following procedure.

Twenty g. of 3,5-dinitro-4-hydroxy-phenylarsinic acid is suspended in 50 cc. of water and dissolved by adding 13 cc. of 40 per cent sodium hydroxide (2 mols.). To this solution is added a solution of 40 g. of magnesium chloride (crystals) in 400 cc. of water, the whole cooled down to 0° and reduction effected by gradually introducing 130 g. of sodium hydrosulphite (commercial powder) with continuous mechanical stirring. During this process, the temperature should not be permitted to rise above 2°, since otherwise further reduction to the arseno compound will occur. When all the hydrosulphite has been introduced, the solution becomes decolorised, and upon continued stirring for 1·5 hours at 0° a white crystalline precipitate of the amino compound appears. This is filtered off and the mother liquor expressed as completely as possible. To purify, the crude product is dissolved by triturating with an excess of diluted hydrochloric acid in a mortar. The solution is filtered, and the filtrate neutralised at low temperature with concentrated sodium hydroxide solution until it is but slightly acid to congo red paper. The precipitate of the pure amino compound is filtered off and washed with cold water until it is free from sulphate and chloride, then with methyl alcohol, and finally with ether. It is dried *in vacuo* over sulphuric acid. The yield (after one purification) is about 8·0 g. or 50 per cent.

*Properties.* — 3,5-diamino-4-hydroxy-phenylarsinic acid is a white crystalline product which darkens during the process of purification. It is soluble in alkalies, also hydrochloric acid: insoluble in methyl alcohol, ethyl alcohol, ether, acetone, chloroform, benzene. Its solution in alkali darkens very rapidly on standing exposed to the air.

Calculated for $C_6H_7O_4N_2As$: N, 11·29; As, 30·24. Found: N, 10·70; As, 29·52.

3-*Amino-4-hydroxy-phenylarsinic Acid.* — This compound was first prepared by Ehrlich and Bertheim by the reduction of 3-nitro-4-hydroxy-phenylarsinic acid with sodium amalgam (*D.R.P.*, 224,953, 1910). Another method in which sodium hydrosulphite is used as the reducing agent has been briefly described in a German patent (*D.R.P.*, 224,953, 1910). Jacobs and Heidelberger (*Jour. Am. Chem. Soc.*, 1918, xl., 1580) prepared this same arsinic acid by the use of ferrous sulphate and sodium hydroxide. The authors in preparing this compound used sodium hydrosulphite as the reducing agent.

Twenty g. of 3-nitro-4-hydroxy-phenylarsinic acid is suspended in 50 cc. of water and dissolved by adding 15 cc. of 40 per cent sodium hydroxide solution (2 mols.). A solution of 40 g. of magnesium chloride crystals in 300 cc. of water is added, the whole cooled down to 0°, and reduced by adding 85 g. of sodium hydrosulphite and proceeding exactly as in the case of the previous compound. The yield of purified product is about 10·8 g. or 61 per cent.

*Properties.*—3-Amino-4-hydroxy-phenylarsinic is a white crystalline substance which during purification turns slightly brown. It is soluble in hydrochloric acid, sodium and ammonium hydroxides; insoluble in acetic acid and the usual organic solvents. Its alkaline solution darkens rapidly on standing in air.

Calculated for $C_6H_8O_4NAs$: N,6·01. Found: 5·74.

*Acetyl-3-amino-4-hydroxy-phenylarsinic Acid.*—Ten g. of 3-amino-4-hydroxy-phenylarsinic acid is suspended in 50 cc. of water, immersed in an ice-bath, and mechanically stirred. Nine cc. of acetic anhydride (one mol equals 4·4 cc.) is gradually introduced, and the stirring maintained for three hours. The whole is filtered, and the precipitate suspended in dilute hydrochloric acid. This removes the unchanged amino compound, the acetyl derivative remaining undissolved. This is filtered off, washed with water till free from hydrochloric acid, then with methyl alcohol, and finally ether. It is dried *in vacuo* over sulphuric acid. The yield is 3·5 g. of pure substance.

*Properties.*—Acetyl-3-amino-4-hydroxy-phenylarsinic acid is a light brown crystalline substance, soluble in dilute alkalies. It is insoluble in hydrochloric acid, acetic acid and the usual organic solvents.

Calculated for $C_8H_{10}O_5NAs$: N, 5·09; As, 27·27
Found: N, 5·10; As, 27·61.

*Diacetyl-3,5-Diamino-4-hydroxy-phenylarsinic Acid.*—This compound is prepared from 3,5-diamino-4-hydroxy-phenylarsinic acid in exactly the same way as the previously described compound. The yield is 75 per cent.

*Properties.*—A pale brown crystalline substance, soluble in sodium and ammonium hydroxides. Insoluble in water, hydrochloric acid, and the usual organic solvents.

Calculated for $C_{10}H_{13}N_2O_6As$: N, 8·43; As, 22·60
Found: N, 8·49; As, 22·98 per cent.

3,5,3′,5′-*Tetra-amino-4,4′-dihydroxy-arsenobenzene Tetrahydrochloride.*—Although this amino compound has been very briefly described in a German patent, its tetrahydrochloride has not been described. It is interesting to note that it appears to exist in two modifications, one easily soluble in methyl alcohol, and the other only sparingly so.

25 g. of the corresponding dinitro-hydroxy-phenylarsinic acid is dissolved in 525 cc. of water to which has been added 16 cc. of 40 per cent sodium hydroxide solution (2 mols.). Reduction is effected by a solution of 575 g. of sodium hydrosulphite and 65 g. of magnesium chloride in 2600 cc. of water. After 1·5 hours' stirring at 55° to 60° the yellow precipitate of the tetra-amino compound is filtered, washed with distilled water until most of the hydrosulphite has been removed, and then dried on porous plates.

To convert the dried base into its tetrahydrochloride, it is introduced into 220 cc. of absolute

methyl alcohol containing hydrogen chloride. About one-half of the tetrahydrochloride dissolves. This is decanted off. The remaining insoluble portion is triturated in a mortar with more ethyl alcohol-hydrochloric acid solution in order to remove the soluble fraction completely. The entire methyl alcohol solution of the tetrahydrochloride is mixed with five volumes of U. S. P. ether. A light yellow precipitate is immediately produced. This is allowed to settle, the supernatant fluid decanted, the precipitate washed several times by decantation with ether, rapidly filtered and finally dried *in vacuo* over sulphuric acid. The yield is 8·0 g.

The undissolved fraction of the tetrahydrochloride is washed with ether and also dried *in vacuo* over sulphuric acid. The yield is 7·5 g.

Both modifications are yellow substances easily soluble in cold water. From this solution the base is precipitated by the addition of sodium hydroxide and redissolved when sufficient alkali has been added to form the monosodium salt. This solution on standing rapidly becomes turbid due to the action of the carbon dioxide of the air. A solution of disodium salt is less readily precipitated. Both salts in solution when exposed to the air, rapidly oxidise, more so than the corresponding salts of 3,3′-diamino-4,4′-dihydroxy-arsenobenzene dihydrochloride.

*Analysis.*—Neutralisation of the hydrochloride and formation of monosodium salt. Soluble modification: subs., 0·100: 9·0 cc. 0·1 *N* NaOH Insoluble modification : subs., 0·100 : 7·5 cc. 0·1 *N* NaOH. Calculated for $C_{12}H_{18}N_4Cl_4O_2As_2.1CH_3OH$ : 8·7 cc. 0·1 *N* NaOH.

Oxidation by iodine.

Soluble modification. Subs., 0·100: 13·50 cc. 0·1 *N* iodine.

Insoluble modification. Subs., 0·100: 13·6 cc. 0·1 *N* iodine.

Calculated for $C_{12}H_{18}N_4Cl_4O_2As_2.1CH_3OH$ : 13·95 cc. 0·1 *N* iodine; 11·16 mg. oxygen Found: Sol. mod., 10·80 mg. oxygen; insol. mod., 10·88.

In view of the fact that this compound cannot be recrystallised, the only method of purification consisting of redissolving in methyl alcohol-hydrochloric acid solution and reprecipitating from ether, we are reporting these results as the best we have been able to obtain thus far.

Calculated for $C_{12}H_{18}N_4Cl_4O_2As_2.1CH_3OH$ : N, 9·76; As, 26·13. Found: sol. mod., N, 8·80; As, 26·62; insol. mod., N 8·80; As, 25·09 per cent.

*Tetra-acetyl*-3,3′,5,5′-*tetra-amino*-4,4′-*dihydroxy-arsenobenzene.*—Two g. of diacetyl-3,5-diamino-4-hydroxy-phenylarsinic acid is dissolved in 7·0 cc. of water by the addition of 4 cc. of 15 per cent sodium hydroxide solution. Two g. of magnesium chloride (crystals), and 10 g. of sodium hydrosulphite are dissolved in 45 cc. of water and immediately mixed with the solution of arsinic acid. The combined solutions are filtered rapidly, and warmed up to 55 or 60°. This temperature is maintained for 30 minutes, during which time the mixture is continually stirred. The precipitate which forms is yellow at first, but at the end of the reduction it appears white. It is filtered off, washed thoroughly with water and dried *in vacuo* over sulphuric acid. The yield is 1·2 g.

The compound is a white powder insoluble in water, dilute hydrochloric acid, and the usual organic solvents, soluble in glacial-acetic acid however. It is soluble in dilute alkalies, forming a yellow solution which is characteristic of arseno compounds; also soluble in dilute sodium hydrogen carbonate solution. Like all other arseno compounds it decolorises iodine, thereby becoming oxidised to its corresponding arsinic acid. This reaction cannot be utilised for its quantitative estimation, thereby differing from other arseno compounds, because of difficulty in distinguishing the exact end-point.

Calculated for $C_{20}H_{22}O_6N_4As_2$ : N, 9·93; As, 26·60. Found: N, 10·14; As, 25·75.

*Diacetyl*-3,3′-*diamino*-4,4′-*dihydroxy-arsenobenzene.*—The method of preparation of this substance from acetyl-3-amino-4-hydroxy-phenylarsinic acid is the same as that of the tetra-acetyl compound described above. The yield is 73·17 per cent.

The substance is a pale yellow powder insoluble in water, methyl alcohol or sodium hydrogen carbonate solution, soluble in sodium hydroxide solution from which it is reprecipitated by hydrochloric acid.

Calculated for $C_{16}H_{16}N_2O_4As_2$, N, 6·22; As, 33·33. Founded: N, 6·16; As, 33·00.—*Journal of the American Chemical Society,* March, 1921.

## MINERAL FERTILISERS IN JAPAN.

The production of pyrites was, in 1912, 82,600 metric tons, and 126,000 in 1913, since when it has increased. Moreover, we must consider the fact, that Japan is a great sulphur producer which favours manufacture of acid. Before the war, the production was, apparently, 30,000 metric tons, which has increased to 70,000. Subsequently to an agreement existing before the war, which was then cancelled and again restored, prices were fixed by a Convention in 1916. Sulphuric acid, as in all other places, is utilised for manufacture of mineral fertilisers, especially superphosphates. Imports of natural phosphates which, in 1913, amounted to 347,000 metric tons, fell to 322,000 in 1914, and even 189,000 in 1915; but the imports for 1916 and 1917 were estimated at 280,000.

However, Japan has developed her phosphate production in the Island of Rasa, Lu Choo, which from 740 metric tons in 1908 rose to 38,259 in 1914; 57,716 in 1915, and 114,810 in 1916.

Although the superphosphates obtained are largely consumed in the country itself, a considerable quantity is exported to Java, where 40 per cent superphosphates are required, and also to Russia. This market was only of interest during the war. It seems possible to greatly develop the utilisation of artificial fertilisers in Manchuria, where they are as yet little employed.

There are three principal manufacturing companies of fertilisers, viz., the Kuhard, the Furukawa, and the Sumitomo Co., the respective annual production being 7,000,000, 4,880,000, and 680,000 bags.

Consumption of sulphate of ammonia is about 140,000 metric tons. chiefly supplied by imports from England (110,000 metric tons in 1910). As during the war these imports almost ceased (20,000 in 1915) the Japanese have remarkably developed the industry.

The production of sulphate of ammonia was

,000 metric tons in 1916, the amount for 1917 eing estimated at 100,000, though really it was nly 57,915, and in 1918 31,444. The German niline Consortium has decided, it is said, to ound a works on the lines of those of Leuna, in apan and the United States for fixation of nitroen by the Haber process.

The employment of potash salts is insignificant; hile nitrate imports were 24,694 metric tons in 914.

The imports of mineral and other fertilisers in 914 represented a value of nearly 80,000,000 ancs. Home production is valued at about 25,000,000 francs, having tripled within the space f ten years.

In spite of this, Japan will probably always be ependent upon imports from abroad for part of ne phosphates, potash salts, and nitrates, as long s manufacture of synthetic ammonia does not neet all requirements.—*L'Industrie Chimique*, May, 1921.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

*Ordinary Meeting, June* 23, 1921.

PROF. C. S. SHERRINGTON, President, in the Chair.

THE following papers were read :—

"*A Study of Catalytic Actions at Solid Surfaces. VI.—Surface Area and Specific Nature of a Catalyst: two Independent Factors Controlling the Resultant Activity.*" By E. F. ARMSTRONG, F.R.S., and T. P. HILDITCH.

The influence of the surface area of a nickel atalyst on its activity has been traced by exmination of the bulk gravity of various types of atalyst: there exists a qualitative relation beween bulk gravity and catalytic activity, the nost efficient catalyst occupying the greatest olume per unit mass.

The rate of reduction in hydrogen of nickel xide prepared in various ways has been examined t various temperatures. A light nickel oxide preared from the precipitated hydroxide gave curves hydrogen consumption/time) showing faint points f inflection at stages of the reduction which aried with the temperature of reduction; whilst ense, fused nickel oxide gave a smoother curve, nd nickel hydroxide deposited on kieselguhr as a upport showed a smooth, continuous curve.

The reduction curves are evidently related to he physical conditions (state of the oxide and emperature of reduction) rather than to the ormation of any definite compounds intermediate n composition between nickelous oxide and nickel.

When a support (kieselguhr) is overloaded with nickel hydroxide and reduced so that varying proortions of the nickel are in the metallic state, he catalytic activity, measured by the hydrogenaion of the unsaturated glycerides, increases apidly to a maximum value, which is maintained hereafter until and when all the nickel hydroxide nas been reduced to the elementary state.

The data given indicate that the activity is dominated by the condition of the surface layer of reduced nickel, since it is obviously this part of the mass which will be first reduced by hydrogen to the metallic state.

"*A Contribution to the Thermodynamical Theory of Explosions—Part I.; and Part II.—A Contribution to the Thermodynamical Theory of Explosions.*" Part I. by Sir J. B. HENDERSON, D.Sc. Part II. by Sir J. B. HENDERSON and Prof. H. R. HASSE.

In this paper modern advances in Chemical Thermodynamics, dealing with dissociation of gases and variation of their specific heats with temperature are applied to the science of internal ballistics, which has been in the past mainly empirical. Direct experiments on specific heats of gases are limited to temperatures below 1500° C., and extrapolation, based upon Thermodynamic Theory and extending to temperatures of 3500° C. and pressures of 20 tons/in.$^2$, tests the theory severely.

Part I. of the present paper, written in 1913-14 by one of the authors, contains the application of these theories to the calculation of the explosion-pressure of cordite in closed vessels, the results being in remarkable agreement with experiment. It also contains the calculation of the curve of adiabatic expansion of the products of explosion by considering a series of states of equilibrium and, following thereon, the ideal indicator diagram of a gun.

During the war confidential publication took place, and the curve of rise of pressure and the maximum pressure allowing for burning of cordite in parallel layers and for varying capacity of chamber during burning, due to movement of the projectile, were then calculated by the authors. The results have proved very useful in practice. They enable the indicator diagram of gun, maximum pressure, and muzzle velocity of projectile to be calculated with remarkable accuracy from the chemical composition of explosive used and rate of burning of the cords. They also show the effects, qualitative and quantitative, produced by variations in the different variables, initial pressure, density of loading, temperature of charge, diameter of cords, &c., and place internal ballistics on a better scientific foundation than formerly. Method and results are also applicable to internal-explosion engines using gas or oil

"*Eddy Current Losses in Cylindrical Conductors, with Special Applications to the Alternating Current Resistances of Short Coils.*" By S. BUTTERWORTH.

The general theory of the eddy current losses produced in a non-magnetic metallic cylinder when placed in a transverse field of any form is developed, and a general series is obtained expressing the eddy-current losses.

From this series conclusions are drawn in regard to the modification of the losses by the want of uniformity of the field over the section of the cylinder.

The theory is applied to obtain an approximate solution of the problem of the effective resistance of two equal parallel wires carrying equal currents either in the same or in opposite directions. The formula obtained is shown to be in good agreement with Kennelly's experimental results.

The "uniform field" theory is applied to determine the effective resistance of parallel wire systems, and, by calculating the mean square field acting throughout the section of the coil,

formulæ are obtained for the effective resistances of single- and multi-layer solenoidal coils either of solid or of stranded wire.

The theoretical results in the case of single-layer solid wire coils at high frequencies are compared with measured values.

From the theoretical formulæ conditions are deduced in regard to the shape of coil and spacing, to employ which will produce the maximum value of L/R′ for a given length of wire of given diameter.

Solid wire coils are compared with stranded wire coils, both being wound under the most efficient conditions.

The observed inferiority of stranded wire coils as compared with solid wire coils at high frequencies is due to the lack of internal spacing of the strands of the coils making the best conditions unattainable.

The theoretical conditions for the minimum effective resistance of a many-layered coil of given inductance and resonating with a condenser of given capacity are worked out.

"*The Currents induced in a Cable by the Passage of a Mass of Magnetic Material over it.*" By E. S. BIELER.

The electromotive force induced in a cable by the passage of a mass of magnetic material over it is investigated in the case where the mass is in the form of a spherical shell. The deflection of a critically damped galvanometer in series with it is deduced.

The results of the theoretical investigation are compared with those of experiments carried out in the laboratory on a small scale, and good agreement is obtained in each case.

In conclusion, the theoretical results are used to determine the law of variation of the galvanometer with different factors, and the relation between the galvanometer deflection and the E.M.F. which produces it.

"*The Experimental Analysis of Sound in Air and Water: some Experiments towards a Sound Spectrum.*" By GUY BARLOW, D.Sc., and H. B. KEENE, D.Sc.

The original sound vibration gives rise to an electric current of telephonic magnitude, which is then analysed by a method of periodic interruption, whereby the frequencies and relative amplitudes of the constituents may be determined, and a "sound spectrum" constructed. A specially controlled motor-driven interrupter, with a range of interruption frequency from 3—2000/sec. is placed in series with a Broca galvanometer in the circuit containing the alternating current to be analysed. The speed of the interrupter is then slowly varied over the whole range of frequency under investigation. When the interruptions synchronise with any component of the current, the galvanometer responds by giving a steady deflection whose magnitude depends on the phase difference, and this latter can be adjusted to give the maximum response. In this way the amplitude of each component may be determined, and at the same instant the corresponding frequency is observed stroboscopically.

Experiments are made (1) to test the reliability of the method by analysing alternating currents containing known constituents; (2) to analyse different types of sound in air, using both carbon microphone and magnetophone receivers; (3) to analyse sounds in water (in a reservoir), for which special sounders and receivers are constructed and describe. The variations of the sound spectrum with distance, depth, and direction are investigated, and the spectrum of a motor-driven boat is obtained under various conditions

"*The Theory of the Analysis of an Electric Current by Periodic Interruption.*" By GUY BARLOW, D.Sc.

This paper contains a mathematical treatment of the methods of periodic interruption used in the experimental analysis of sounds described in the previous paper, together with an expansion of the effects of periodic interruption on the intensity and quality of sounds heard in a telephone.

## SOCIETY OF GLASS TECHNOLOGY.

THE last meeting of the Society of Glass Technology for the session 1920-21 was held in the Applied Science Department, The University, Sheffield, on Wednesday, June 15, 1921, at 2.30 p.m., the President, Dr. MORRIS W. TRAVERS, F.R.S., in the Chair The initial formal business included the election, under rules recently adopted, of Prof. P. G. H. Boswell, O.B.E., D.Sc., D I.C., F.G.S., Professor of Geology in the University of Liverpool, as the first Honorary Member of the Society.

The meeting resolved itself into a discussion on the subject of "Oil Firing in the Glass Industry." The President, in opening the subject, said that he would restrict his own remarks to the consideration of the efficient utilisation of energy in two types of furnaces. If one purchased oil or coal, one actually purchased energy which might, or might not, be represented by the calorific value of the fuel. What one really had to consider was the energy available for melting glass or for other similar purposes.

He showed, by means of thermo-chemical calculation that the relative fuel efficiency of a furnace in which the oil was burned with air at the ordinary temperature, and of a furnace in which coal was first gasified by air with only a little steam, the gas being burned with air at the ordinary temperature were practically identical. That non-regenerative glass tanks fired with oil were preferred to those fired by gas was due to the fact that small gas-fired tanks were probably inefficient. He left the consideration of such questions as capital cost, working expenses, and control to other speakers.

In oil-firing practically the whole of the air could be pre-heated, but in gas-firing only the secondary air could be pre-heated, so that a regenerative oil-fired furnace was more efficient than a furnace in which the secondary air was pre-heated. Other conditions being equal, the ratio of the efficiency of the oil and gasified coal systems was as 1·37 to 1. The results might be summed up as follows:—

| | Net calorific value. | Cost in London per ton. | Efficiency of combustion. | Relative cost. |
|---|---|---|---|---|
| Oil | 10500 | 105/- | 1·37 | 1·20 |
| Coal | 7420 | 45/- | 1·00 | 1·00 |

This did not take into account the other factors to which he had referred which favoured the use of oil.

Mr. J. CONNOLLY remarked that one of the chief points to be considered was the price of the

oil. It had undoubted advantages in respect of ease of handling, reduced storage room required, less staff, and less expensive furnace construction He had run an oil glass furnace for four years. It worked with fewer breakdowns and stoppages, and more pleasantly than any other method. At the end of that period, however, the price of oil was "gingered up," and the use of the oil was abandoned. The adaptability of oil to glass work had been demonstrated, and was past argument, but he did not think they would get a higher efficiency with oil than with coal, so long as there was a great difference in price. There was a more steady dependence on the price of coal than of oil.

Mr. J. H. STEELE thought that oil had not been given a fair chance in the glass industry. His own experience of it was very satisfactory It was unusual, however, to find a glass furnace properly adapted to oil consumption. He had known better results to be obtained from the use of crude oil or creosote than from fine petroleum of high calorific value; a fact which indicated that the furnaces in use were not satisfactory.

Mr. F. G. CLARK spoke of the use of "glory holes" fired by oil. The best results were obtained from crude creosote oil, partially heated, and compressed air at about 15lb. to 20lb. pressure per square inch. In making 8oz. bottles on a 7½-hour shift, some 3·92 gallons of oil were used, at a cost of 4s. 3d. per shift. When two chairs were working at one glory hole, the cost worked out at about 2s. 2d. per shift. Gas did not yield the temperature desired, and creosote oil gave a fuller and "fatter" flame than did petroleum. Consequently the neck of the bottle was heated up more uniformly, and much better finished work was produced.

Mr. G. F. LAWTON described a simple oil burner that had yielded good results. In one power station 1 ton of oil was apparently equivalent to about 2½ tons of coal. They must consider very carefully the construction of the furnace and the proper application of the oil.

Mr. J. VENN STEVENS pointed out the advantages of oil fuel for glass furnaces. It was clean to use. Besides, the flame came into direct contact with the glass without producing any discolouration or deterioration. The temperature could be maintained uniform, thus saving many articles which would be ruined by the fluctuations of temperature due to unsteady firing.

Mr. A. BAYLISS remarked that the *Aquitania* had in the stokehole 350 men when fired with coal, but only 84 with oil fuel. With solid fuel the efficiency might range from 50 per cent to 65 per cent. In the case of oil fuel the efficiency might be as high as 85 per cent. In addition, there was instantaneous ignition and extinction. The freedom from sulphur in the gases formed by combustion was an important point for glass workers.

Mr. W. H. CASMEY referred to the very great potentialities of oil when mixed with inferior qualities of solid fuel. In one case by taking 3 tons of coke breeze (at 12s. 6d. per ton, calorific value 10,000 B.Th.U.) and one ton of oil fuel, a combined fuel of 12,000 B.Th.U. was secured, equalling 37s. 4d. per ton, and capable of giving an evaporation of 530lb. per 1s., or nearly 2,000lb. more evaporation per ton than with coal only at 40s. per ton.

Mr. W. J. REES thought it was very necessary for some reliable figures to be obtained showing how efficient coal-firing was compared with oil-firing.

Prof. W. E. S. TURNER read a communication from Messrs. Stein & Atkinson, Ltd., and a diagram was exhibited and explained showing the proposed design of a combustion chamber for the oil-firing of a glass tank furnace. Prof. Turner also read a communication from Messrs. Shell-Mex, Ltd., in the course of which it was stated that there were very few oil-fired pot furnaces in this country. The few that had been tried had not been entirely successful, the chief trouble being the cracking of pots. This was due to excess of heat in one particular place on the pot, causing unequal expansion. A method of avoiding this was suggested.

The discussion was continued by other speakers. Burners or drawings of plants were also exhibited by the following firms .Messrs. Alldays & Onions, Ltd., Birmingham, Anglo-American Oil Co., Ltd., London, Holdsworth & Sons, Ltd., Bradford, Kermode's Ltd., Liverpool, Lawton Machine Tool Co., Sheffield, White Patent Oil-burning Co., Ltd., South Shields, J. Samuel White & Co , Ltd., Cowes, Isle of Wight.

## PHYSICAL SOCIETY.

*June* 10, 1921.

DR. C. H. CHREE, F.R.S., Vice-President, in the Chair.

A LECTURE on "*The Stability of Atoms*" was delivered by Prof. SIR ERNEST RUTHERFORD, F.R.S.

The lecturer commenced by referring to the earlier work in which attempts at the disintegration of atoms had been made. Traces of hydrogen and helium had been found in discharge tubes believed to be initially free from these gases; but it was clearly impossible to establish that no source of contamination was available, and that the results were due to disintegration of the atoms of other substances.

The properties of the nucleus atom were then recalled and the method of attack most likely to succeed in breaking it up was discussed. It is easy to remove electrons, but these are replaced almost immediately and the atom remains as before.

It is necessary therefore to attack th enucleus, and to do this successfully requires extremely swift particles.

Slides were shown illustrating the effects produced when $\alpha$-particles fired through hydrogen collide with an atom, and experiments were illustrated and described from which the conclusion had been drawn that when an $\alpha$-particle collides with a nitrogen atom, a hydrogen atom is expelled from the nucleus. The speed of these is in excess of what can be obtained by collisions in hydrogen gas itself, so that the result cannot be accounted for by contamination of the nitrogen with hydrogen, but must be due to the disintegration of the nitrogen nucleus.

Recent results on the disintegration of aluminium and other elements were briefly indicated.

The CHAIRMAN expressed the thanks of the Society to SIR ERNEST RUTHERFORD for his

address. Queries were put by Dr. Andrade, Dr. Owen, and Dr. Rayner, to which the Lecturer replied.

## MINERALOGICAL SOCIETY.

*June* 21, 1921.

DR. A. E. H. TUTTON, Past-President, in the Chair.

*"A Note on Crystal Measurement."* By Dr. H HILTON.

It was pointed out that considerable labour could be saved by measuring the angles between zones through two faces instead of the angles between zones through one face and the angels between this face and the rest. A point of geometrical interest in connection therewith was also discussed.

*"The Trend of Reconstitution Processes in Shales, Slates, and Phyllites."* By A. BRAMMALL.

The author correlates microscopical data with data deduced from chemical analyses. The finely powdered rock is extracted with (a) 20 per cent hydrochloric acid; (b) 50 per cent hydrochloric acid, and these extracts are analysed and discused with reference to the molecular proportions of the bases present. The residual slime is treated with dilute hydrofluoric acid, freed from silica gel, and thoroughly washed. Free carbon particles are floated off by the froth produced on vigorously shaking up the slime in a flask half full of water, to which a few drops of amyl alcohol, paraffin, and sodiu msilicate have been added. Samples of coarse-grade and fine-grade sericite are separated by elutriation and analysed. Heavy or insoluble residues are obtained and examined. In this paper, data referring to Bolivian rocks (collected by Dr. J. W. Evans), and, for comparative purposes, to the Skiddaw Slate, are discussed. Work on the rocks of North Devon and North Wales is in progress. Trend, in general, is towards the establishment of a metastable ternary system of white mica, chlorite, and quartz, by a process of molecular differentiation: (a) Monad-oxides, type $R_2O$ allied with alumina, silica, and water (mica); (b) diad-oxides, type RO, allied with alumina, ferric oxide, silica and water (chloritic matter); and (c) free silica (quartz). In the early stages this differentiation is imperfect; the mica contains iron oxides, magnesia, &c , and the chloritic matter adsorbs alkalies. The identity of mineral species evolving from the chloritic matter depends partly upon the molecular ratio $R_2O_3 : RO$, and this in turn depends partly upon the reduction of ferric oxide to ferrous oxide. The development of rutile, ilmenite, epidote, &c., is probably subordinate to the main trend.

*"The Micropetrography of the Rock-Gypsum of Nottinghamshire."* By W. A. RICHARDSON.

Microscopic examination reveals a wide range of structural types, including many metamorphic types. The evidence supports the view of B. Smith that the main series is of sedimentary origin, and that the nodular deposits are segregations. The metamorphic effects appear to be due to pressure caused by the partial or complete hydration of the anhydrite.

## OBITUARY.

### Mr. A. P. SINNETT.

WE regret to announce the death of Mr. A. P. SINNETT, Vice-President of the Theosophical Society, which took place at his residence in Ladbroke Grove, on June 25. Mr. Sinnett was an old friend of Sir William Crookes, and a well-known writer on theosophical matters. For many years he has been a familiar figure at the meetings of the Royal Institution. He was of a quiet, kindly disposition, and was respected and esteemed even by those who failed to agree with many of his conclusions.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences.* Vol. clxxii., No. 25.

"Absorption of Oxides of nitrogen by Nitric and Sulphuric Acids."—By A. Sanfourche.

"New Magnesium Hydraulic Cement"—By A-Ch. Vournazos.

"Catalytic Decomposition of some Polyhalogen Aliphatic Hydrocarbons."—By Alphonse Mailhe.

"Catalytic Decomposition of Bromacetic Acids, and of some mixtures of Bromine and Acetic Acid."—By J. B. Senderens and J. Aboulenc.

"Distribution of the Saline Substances and the Mineral Elements in Milk."—By Ch. Porcher and A. Chevallier.

## NOTES.

ROYAL INSTITUTION.—A General Meeting of the Members of the Royal Institution was held on the 4th inst., Sir James Reid, Vice-President in the Chair. Miss F. E. I. Smythe and Mrs. A. J. Webbe were elected Members. The Chairman announced that the Managers had re-elected Sir James Dewar Fullerian Professor of Chemistry.

THE Library of the Chemical Society will be closed for Stocktaking from August 1 to 13 inclusive, and will close each evening at 5 o'clock from August 15 to September 10.

THE recently-formed Glass Research Association has issued its first bulletin in the form of a confidential communication to its members The publication consists of a booklet of some 43 pages, well illustrated with photographic reproductions, and constitutes a fine record of work. Papers upon the cause of Cords in Glass, the nature and cause of Bloom and Dimming on Lamp-blown Glassware, new Microfurnace for Glass Examination at High Temperature, and the purification of Mercury for use in Thermometers, are recorded. Notes on Abrasives, the effect of Chlorides on the Melting and Working of Lead Potash Glass, Refractories, &c. Experimental work in glass-making upon a large scale will be carried out at the Sheffield University under the supervision of the Director or Research, Mr. R. L. Frink, in collaboration with the members of the various re-

search committees that have been formed to deal with special questions. The Association appears to be dealing with the important problems of the British Glass Industry in a practical way, and the result of its labours will have great influence upon the future of British glass manufacture.

An Exhibition, to take place at the Crystal Palace between September 1 and October 22 is being organised, with the title of the "Co-Partnership Exhibition," and one of its objects is to record the remarkable movement that has been made in recent years to promote industrial peace between employers and employed.

We learn from the *Scientific American* that Dr. Charles Benson Davis, of New York City, claims that he can make the Elements, gold, silver, copper, and platinum by transmutation of the common element. Dr. Davis is said to be a Fellow of the more important English and French Scientific Societies, and has requested the Engineering Foundation in New York City to investigate his claims. We shall naturally be interested to hear the result.

We have received from the Managing Director of the British Road Traffic Association a copy of the new Motor Time Table, the Motor A.B.C., which gives full particulars of the daily motor service, compiled in such a way that it is perfectly simple for anyone wishing to travel by motor-coach to find in a few minutes exactly what services are available on the route he wishes to use, the starting point, starting time, fares, and booking office for each coach, and he is able to make his arrangements with the least possible delay or worry. This method of travelling is becoming increasingly popular, and great changes will undoubtedly take place in the near future In addition to motor services, the A.B.C. gives, the Aeroplane facilities, together with fares, &c. The Motor-Coach A.B.C. is published by Messrs. E. J. Larby, Ltd., 30, Paternoster Row, E.C., price 6d.

The Telephone Service. — Messrs. Geo. Wheatley & Co., Ltd., have published and will supply free on application to their London Offices, 95, Upper Thames Street, a useful little booklet showing at a glance the new method of "charging by distance" between subscribers connected with the Exchanges within the inner London Zone, as well as the cost of a call to points outside the 1½ limit within a radius of 25 miles of London, and other data of value.

Refractory Material.—Roast recommends a mixture of Greenwille magnesite burnt at 1700° C. and magnesium chloride as an excellent refractory material. One application of magnesite is for manufacturers of Sorel cement a mixture of magnesia and chloride of magnesia forming a vitreous block of oxychloride. Substances like sawdust or sand can be incorporated to make very sound, strong floors without grooves. It is also employed for manufacture of magnesia bisulphite to prepare wood pulp for paper, precipitated carbonate of magnesia for pharmaceutic products, insulating steam pipes, and finally, as a base in electrolytic preparation of magnesium for alloys, especially with aluminium.—*Industrie Chimique*, March, 1921.

Formation of Hevea Latex in the Hevea Brasiliensis.—The globules of latex, according to W. Bobiloff (*Archief Rubber Cultuur*, 1919, 3374), derived from the mature parts (trunk, &c.) of the Hevea, usually comprise four kinds, viz., (a) round, very small globules, diameter $0{\cdot}5\mu$; (b) round, larger globules, diameter $1$—$2\mu$; (c) pear-shaped globules with tail, diameter $1{\cdot}5$—$2\mu$; (d) pear-shaped globules, diameter $1{\cdot}5$—$3\mu$. There are only very small round globules in the branches, leaves, and young roots. M. Bobiloff concludes that the latex in new branches is quite independent of that in the remainder of the tree, and that the latex forms in the laticiferous tissue itself.—*Le Caoutchouc*, February 15, 1921.

Chemical Action of Light.—At the request of Ciamician and Silber, Sig. E. Sarnagiotto made researches on the chemical action of light. The results are summarised as follows. The property of autoxidation of oxalic acid in light is associated with oxidation of ethyl alcohol and glycerin. Thiophene undergoes autoxidation in light. Dibenzyl and benzophenone are condensed in benzophenone-pinacone and triphenylbenzylethanol. Quinone and toluene reacted under the action of light in a confused way. However this may be, the quinone was transformed into a brown resinous mass accompanied by some crystals of hydroquinone and quinhydrone. Toluene left traces of benzoic aldehyde. The acetone and amyl alcohol gave a resin and various compounds: (1) Dimethylisobutylenic glycol; (2) Isopropylbutylcetone; (3) Diisobutylethylenic glycol. —*Gazz. Chim. Ital.*

## NEW COMPANIES.

The under-mentioned particulars of New Companies recently registered are taken from the Daily Register compiled by Jordan & Sons, Limited, Company Registration Agents, Chancery Lane, W.C.2.

Faulkner's Drug Stores, Limited.—(175308)—Registered 21st June, 1921. 1, Church Street, Cobham, Surrey. To acquire and carry on the business of Drug Stores. Nominal Capital: £500 in 500 Ordinary Shares of £1 each. Directors. H. B. Faulkner, 1, Church Street, Cobham, Surrey: (Managing Director); H. Ivimey, 4, Priory Road, Hastings; L. Whitehouse, 319, Stratford Road, Sparkbrook, Birmingham. Qualificaiion of Directors: 1 Share. Remuneration of Directors: To be voted by Company.

Morgan Brothers (Chemists), Limited.—(175381)—Registered 24th June, 1921. 1, Strand Buildings, Ystradmynack, Glamorganshire. To acquire and carry on the business of Chemist and Drug Store Proprietor. Nominal Capital: £2,000 in 2,000 Ordinary Shares of £1 each. Directors: To be appointed by Subscribers. Qualification of Directors: 1 Share. Remuneration of Directors: To be voted by Company.

James Johnstone & Company, Limited.—(175353)—Registered 23rd June, 1921. Abbey Hey Lane, Gorton, Manchester. To carry on the business of Chemists, Druggists, Oil and Colourmen, etc. Nominal Capital: £2,000 in 2,000 Shares of £1 each. Directors: James Johnstone, 132, Hyde Road, Gorton, Manchester. (Paint Manufacturer); John Johnstone, 132, Hyde Road, Gorton, Manchester: (Paint Manufacturer). Qualification of Directors: £50. Remuneration of Directors: To be voted by Company.

H. J. Parsons, Limited.—(175335)—Registered 22nd June, 1921. Market Place, East Street, Ilminster. To acquire and carry on the business of General Chemists and Druggists. Nominal Capital: £2,000 in 1,500 Ordinary Shares and 500 8 % Preferred Shares of £1 each. Directors: H. J. Parsons, East Street, Ilminster; I. J. Morgan, The Butts, Ilminster. Qualification of Directors: 1, Share. Remuneration of Directors: To be voted by Company.

Shepperleys, Manufacturing Chemists, Limited.—(175290)—Registered 20th June, 1921. To acquire and carry on the business of Wholesale and Retail Chemist and Druggist. Nominal Capital: £30,000 in 20,000 Preferred Shares and 10,000 Ordinary Shares of £1 each. Minimum Subscription: 7 Shares. Directors: J. R. Hex

43, Chancery Lane, W.C 2; P. B Symonds, The Mount, Symonds Yat, Ross-on-Wye; J E. Shaw, Middle Pavement, Nottingham, C. Middleweek, Emerson Lodge, Sherwood, Nottingham. Qualification of Directors £5500. Remuneration of Directors. To be voted by Company.

WALESWOOD COKING COMPANY, LIMITED.—(175295)—Registered 20th June, 1921 Waleswood Collieries, Near Sheffield To acquire and take over as a going concern the business of Manufacturers of Coke and Residuals or by-products of Coal heretofore carried on by Skinner & Holford, Limited Nominal Capital £100,000 in 100,000 Shares of £1 each Directors J H Ashton, Newlands, Todwick, Near Sheffield, A. E. Bond, Lloyds Bank Chambers, New Street, Birmingham; A. Thompson, Throapham House, Throapham, Near Rotherham, S C Skinner, Throapham Manor, near Rotherham. Qualification of Directors 1 Share. Remuneration of Directors: To be voted by Company.

## New Patents.

THIS List is specially compiled for the *Chemical News* by Messrs Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W C 2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications*

16320—Chambers, E V.—Treating waste, etc., liquors containing ferrous chloride. June 14.
16526—Maeder, H.—Process for preparation of tropinone-mono-carboxylic acid esters. June 15
16743—Mau, W —Manufacture of concentrated hydrogen peroxide solution. June 17.
16248—Toniolo, C —Drying or eliminating water vapours from nitric or nitrous acid vapours from gases derived from oxidized ammonia. June 13
16265—Volart y Jubany, R —Manufacture of hydrochloric acid. June 13.
16368—Durand & Huguenin Akt-Ges.—Manufacture of halogen derivatives of basic acridine dye-stuffs June 18.

*Specifications published this Week.*

164374—Dreyfus, H.—Manufacture of cellulose derivatives.
164384—Dreyfus, H.—Manufacture of products having a basis of cellulose derivatives.
137529—Bielouss, E.—Process, for the production of amino-compounds from trinitrotoluol.
164627—Unione Italiana fra Consumatorie Fabricani Di Concumie Prodotti Chemical & Sonneck, A.—Manufacture of sulphuric acid.

*Abstract Published this Week.*

*Catalytic Hydrogenation of Fats, etc.*—Mr. E. R. Bolton of Milner Street, London has obtained a Patent No. 162370 for an improved treatment of fats, etc., in which the catalyst for use in the hydrogenation of fats or oils consists of nickel wool which has been activated by the action of an acid such as nitric acid upon its surface, followed by conversion of the layer of nickel salt to oxide and reduction in hydrogen. The reaction chamber is packed with the activated nickel wool and the oil and hydrogen passed through in counter-current. After use the catalyst is regenerated by first removing nickel soaps by washing with the hot oil, then removing the oil by solvents and finally heating in hydrogen. According to the provisional Specification, the nickel wool may be activated by alternate oxidation and reduction, the catalyst may be electrically heated, and a number of reaction vessels may be arranged in series

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

# NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemical Apparatus, &c., for review or notice to be addressed to the EDITOR.

**SUBSCRIPTIONS,** £1 12s per annum, payable in advance, should be addressed to the MANAGER.

**BACK NUMBERS and VOLUMES** can be purchased on application to he MANAGER.

THE CHEMICAL NEWS,
97, SHOE LANE, LONDON, E.C 4.

## ADVERTISEMENTS.

**All communications for this Department should be ad dressed to—**
T. G. SCOTT & SON,
63, LUDGATE HILL, LONDON, E C.4.

## THE UNIVERSITY OF MANCHESTER

THE Council is about to proceed to the APPOINTMENT of a SENIOR LECTURER or LECTURER, according to qualifications, in PHYSICAL CHEMISTRY, who would be expected to enter on his duties on September 29th, 1921 Commencing stipend £400 and £350 per annum respectively. Further particulars may be obtained from the Internal Registrar.

Applications, giving three references, should be sent to the Internal Registrar not later than July 18th.

Testimonials (one copy of each, which need not be printed) may be submitted.

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THE CHEMICAL NEWS.
VOL. CXXIII., No. 3196.

## PAPER-PULP SUPPLIES FROM INDIA.*

By WILLIAM RAITT, F.C S
Cellulose Expert to the Government of India, attached to the Forest Research Institute, Dehra Dun, India

IT is a commonplace observation now that the question of the world's paper supply has arrived at an acute stage. We see it referred to in more or less lachrymose tones in almost every newspaper we take up. Our pockets test it daily in handing out twopences instead of pennies; the fivepenny five-quire packet, with twopence for twenty-five envelopes, and the halfpenny newspaper have disappeared; and we are studying economy in a direction we never thought of before.

In 1913, the world's consumption of paper was estimated at ten million tons annually, increasing at the rate of 25 per cent every ten years. It must be now nearly twelve millions, or would be if the supplies were available. Of this about 80 per cent is produced from wood—coniferous wood, and preferably spruce. In 1913, although there had been a slow but gradual appreciation of values during the previous ten years, it was still possible to deliver chemically-prepared pulp in this country at £9 to £10, and mechanically-prepared, or ground wood-pulp, at £5 10s. to £6 per dry ton, and newsprint paper could be produced for a penny per pound. Now values are four to five times these figures. The causes stated in order of their importance from lesser to greater are these :—

(*a*) The slow but gradual rise of values in pulp and all that it depends upon, dating from the period of lowest prices, about fifteen years ago. During the war this was, by reason of controls, restrictions, and reduced consumption more or less in suspense, but has now fallen on the industry with five years' cumulative effect.

(*b*) The universal appreciation in value of timber for constructional purposes. The sawmill is now a better market than the pulp factory.

(*c*) Effects of the war in permanently increased costs for labour, freights, fuel, and machinery, and equipment.

(*d*) The total cessation of six years past of manufacturing expansion.

(*e*) The demand for wood has outrun the supply. The trees will not grow as fast as they are cut.

The last of these is the root cause of the trouble and is a constantly increasing menace. It does not necessarily imply that he world's stock of timber has been seriously depleted, but it does mean that forests most favourably situated for exploitation—the areas which produced the penny per pound newsprint—have been largely reduced in productiveness and in many instances destroyed for ever. Expansion in wood-pulp production must seek its supplies at greater distance and increased cost. Notwithstanding this, the new values of pulp, making all allowances for temporary inflation, render such expansion abundantly justified. How much greater, therefore, is the justification for the introduction of a material which is one of Nature's waste products, which reproduces itself naturally and rapidly, for which no sawmill competes, and which offers itself at Nature's valuation, which is next door to nothing.

So we ask ourselves the question, what can India do to fill the gap which has been created? The answer is a great deal, though not so much, perhaps, as is sometimes assumed. When the threatened shortage of paper supplies began to be agitated, some fifteen years ago, an eminent scientist issued what was intended to be a reassuring statement to the effect that "a paper famine was unthinkable, because paper could be made from any vegetable substance, and the world teemed with that." The dictum was seized upon by the Press and circulated round the world, and, no doubt, brought comfort to many anxious consumers. But like many other assertions of many other eminent scientists, it was considered as cold fact, perfectly true, and at the same time, considered as a practical contribution to a difficult problem, perfectly misleading and fallacious Paper can be made from any vegetable substance, but money cannot, and the paper-maker has a quite natural reluctance to make paper unless he can transform it into bank notes. But our eminent scientist's utterance gave rise to a whole crop of wild-cat proposals to make paper from everything, anything, and sometimes bordering on nothing. Nature, however, is not so fantastically generous as that. He whom she would favour must delve into her secrets slowly, deeply, carefully; hoping all things, proving all things, until finally he can hold fast to that which is good. This has been in essence the principle upon which the investigations of the Indian Forest Research Institute, to which I am about briefly to allude, have been carried on. We have thought it more important in the early stages of our proceedings to save people's money than to teach them how to make it, for nothing is more fatal to a promising industry than a disastrous failure at its start. At the same time, while paying considerable attention to the how-not-to-do-it programme, and weeding out the "duds," we have met with encouraging success on the positive side. Our eminent scientist was an all-in, whole hog, hundred per cent man. We have knocked ninety-five off that, but remain quite pleased with the five which have survived. The truth is that out of the hundreds of thousands of species available, a large number have to be rejected because of the cost of isolating their cellulose, a further large number because the cellulose is no good when you have got it, not to mention others which grow in economically inaccessible situations or are too valuable for other purposes. The net result is that so far we have found only two small groups, both belonging to the Gramineæ, which are economically sound as regards the quantity and quality of their cellulose, and the manufactring conditions under which they can be exploited. These are bamboos and a few Savannah grasses. But, though few in number, in the aggregate they mean something considerable. It is, I think, a modest estimate to say that from bamboo, taking only that which is available under *possible* manufacturing conditions, Burma, Bengal, and South-West India could produce ten million tons of pulp per annum, and Assam, from Savannah grasses, three million. India could, therefore, produce pulp for the whole world.

*From *Journal of The Royal Society of Arts*, June 24, 1921. (By permission).

Consider also the growth conditions under which this is obtainable. To grow a spruce or fir tree of pulpwood size takes from 40 to 60 years, with the result that a factory which may at its start have its supplies at its back door finds these year by year receding into the distance with constantly increasing transport costs. Bamboos and grasses come to maturity as yearly or eighteen monthly growths, and all you have to be careful of is not to reduce the reproductive vigour of the plant by too frequent cropping. With bamboo this may mean a three to five year rotation of cropping, and with grasses two to three years. We must, therefore, have a sufficient area to exploit to allow of these rest periods, but that only means that for a ten-thousand-ton pulp output per annum, with average figures for yield and rotation, a 20,000-acre reserve will keep a factory going in perpetuance—a vastly different condition of affairs from those governing a wood-pulp installation which lives on its capital from the start or must adopt a reafforesting policy, which reacts badly upon costs.

Bamboo for paper-making is no new suggestion. In the seventies the late Thomas Routledge, well known as the successful pioneer of esparto grass, experimented with it, obtaining encouraging results as far as quality and suitability were concerned, but failing on the economic side, partly because of its resistance to bleaching, but chiefly because just at that moment wood-pulp came in with a rush and more than filled the demand. In 1905 Mr. Sindall, at the instance of the Government of India, carried out an extensive investigation in Burma, with results considerably more encouraging than those of Routledge, though still somewhat disappointing on the bleaching side, and, at that date, cheap wood-pulp still controlled the market. In 1909 the Government of India, at the instance of Sir John Miller and Sir Robert Carlyle, who succeeded him as Member of Council for Revenue and Agriculture, deemed the time had arrived for a thorough enquiry into the whole subject, and handed it over to the officers of the Forest Research Institute, then under the Presidency of Mr. R. S. Pearson, conducting the Forestry side of it. The chemical branch was begun at the Allahabad Exhibition of 1910, under the Presidency of Sir John Hewett, then Lieut.-Governor of the United Provinces, and the directorship of Mr. P. H. Clutterbuck, Conservator of Forests, and afterwards continued at the Forest Research Institute. Hitherto the Institute's laboratory work has been supplemented by tests at paper mills, by the courtesy of their owners, but Government has new ordered in Scotland a complete pulp and paper-making plant on a sufficient scale to permit of factory methods being used. This is to be erected at the Institute, and will immensely reinforce its usefulness. I would like in passing to call attention to Government's policy in thus carrying out the enquiries initiated by Sir John Miller, Sir Robert Carlyle, and Sir John Hewett, as an evidence of its keen interest in the industrial development of the country.

The chemical branch of the enquiry was begun under conditions considerably more favourable than those with which Routledge and Sindall had to work. The uncertainties on the forestry side had been largely cleared up by Mr. Pearson's work, so there was no longer the risk of wasting time and effort on species and areas which he had shown to be of doubtful value. Considerable improvements had been arrived at in digestion methods, and particularly in the recovery and re-use of soda from the waste liquors, largely reducing the cost of chemical treatment. In Routledge's time a recovery of 40 per cent was regarded as good; now from 80 to 90 per cent is not unusual Most important of all, market values of wood-pulp were no longer on the down grade, and the call for a new source of supply was becoming insistent. The problems to be faced were mainly those concerned with the cost of bleaching. It was evident that the dark brown colour of the unbleached pulp hitherto produced was not its natural and unadulterated colour, which in carefully prepared samples is a light grey, faintly tinted with brown. The dark brown was a degradation result produced by the re-absorption by the *Cellulose*—which, as evidenced by its use in blotting paper, is one of the most absorbent substances known—of some of the complexes produced by the combination of soda with the solubles in the raw material. The first step in the enquiry, therefore, resolved itself into the isolation and separate examination of these This resulted in the separation of the plant constituents into a series of groups, based on their degrees of solubility. Each of these groups is a complex one, exhibiting the group substance in several forms and types, all of which are of interest to the organic chemist, and upon which much valuable work has been done by Cross and Bevan and others—in fact, it is upon the foundations laid by Cross and Bevan that our work has been built—but what interests the pulp manufacturer chiefly is the problem of getting into solution the non-cellulose constituents of his raw material.

Proceeding on these lines, it was found possible to separate the plant constituents into four groups having marked and striking differences of solubility. In order of solubility beginning with the least resistant they are:—

GROUP I.—*Starch* and its secondary and transformation products—all soluble in boiling water.

GROUP II.—*Pectose* soluble in one to two per cent caustic soda solution at boiling temperature

GROUP III.—*Lignin* soluble in four per cent caustic soda solution at temperatures over 130° C.

GROUP IV.—*Cellulose*, the insoluble residue.

An average analysis of bamboo on these lines will give results in round figures as follows:—

| | Per cent. |
|---|---|
| Starch group | 12 |
| Pectose ,, | 20 |
| Lignin ,, | 15 |
| Cellulose ,, | 53 |
| | 100 |

There is also a trifling amount of wax and silica in the cuticle which goes into solution with the Pectose group.

The characteristics of the three soluble groups in their behaviour with soda are as follows:—

*Starch* in its primary form gives a clear colourless solution, but its quantity present in a total group content of 12 per cent does not exceed a sixth. The other 10 per cent of secondary starches form a dark brown nearly black solution of great pulp staining power. The *pectoses* yield a dark brown staining solution which is gelatinous, and therefore powerfully resistant to removal by washing prior to bleaching the pulp. The *lignins* give

a pale brown or amber coloured solution, clear, limpid, and not gelatinous, so that its faint stain is removable by washing. Now, since the raw material does not break down into pulp, and *therefore into a condition permitting re-absorption,* until the lignin has been removed, the next step seemed clearly indicated, viz., remove the substances which produce the objectionable stain on the pulp *before you attack the lignin.* It is fortunate that Nature has made her arrangements to facilitate such a separation process. She gives a beautifully graduated ascending scale of solubilities combined with a descending scale of staining effects. Had the opposite condition prevailed, had the most resistant, lignin, been also the worst staining factor, we should have come up against a dead end.

Cellulose and lignin in combination form that old acquaintance of our school days, woody fibre, yet the analysis is very dissimilar from that of the substance we usually describe as wood, which has a much larger proportion of lignin. The pectose group is replaced by a comparatively small content of resins and gums, while the starch group is barely recognisable in a small percentage of mucilage. The large quantities of starch and pectose found in bamboo and in all Gramineæ, are not in combination with the lignified fibre, but represent stages of transformation in the plant's laboratory of the primary food substance, starch, into the ultimate permanent products, lignin and cellulose. In speaking of lignin as a group, some qualification is necessary. It certainly exists in several types of varying resistance, but not necessarily in the same plant. It is the substance which gives rigidity and resistance to the cellulose against the opposing forces of wind, rain, and decay, and it does not appear likely that Nature wastes effort in providing annual grasses with a protecting medium of the same resistance as that necessary for a tree which may live for centuries, and this hypothesis is borne out by facts. Thus, esparto grass, which exists for a few months, has only about 6 per cent of a lignin which is capable of reduction at temperatures below 130° C., and may even be dealt with by strong soda solutions and prolonged treatment at ordinary boiling temperature, whereas wood may contain as much as 40 per cent of a lignin which is strongly resistant to great density of soda at temperatures as high as 170° C. Bamboo, the life of which is not more than 30 years in the case of the longest-lived species, is provided with a lignin intermediate to these in quality, capable of attack at 130° C., although not fully soluble under 150° C.; the difference between these figures being probably due to physical causes related to penetration of the reagent into a dense, compact, and colloidally protected structure.

From these results we evolved the process which has been called Fractional Digestion, to distinguish it from the earlier method of overhead digestion—"overhead" in the sense that all solubles are dealt with together by a treatment drastic enough to secure the resolution of their most resistant member, and therefore, unnecessarily severe for the less resistant groups, which leaves the pulp steeped in a residual liquor, containing all the objectionable staining matter referred to Such a system has for long been recognised as scientifically unsound, and we think we have proved it to be also economically unsound. It must necessarily be conducted with a large and wasteful excess of soda, first, because the lignin is not attacked until the digestion temperature has risen above 130° C., at which stage the starch and pectose groups have already been brought into solution, and have neutralised a considerable amount of the soda. That which remains will not be of sufficient strength to deal effectively with the lignin unless the original liquor contained a large excess In this connection it is well to bear in mind the effect which density has upon the activity of soda solutions. You may have present the total quantity of soda necessary to effect your object, but if it is distributed throughout so large a volume of water that density is reduced below a certain well-marked degree you will not get the result you wish. A notable example of this is provided in the mercerisation of cotton cloth. The minimum density we have found necessary to give rapid and effective resolution of the lignin of bamboo is that represented by a 4 per cent solution of standard caustic soda, and it must be of this density at the point at which the attack on lignin is commenced. Under the limitations of the overhead method, it will not be of this density at that point unless it carried, at the beginning of digesion, a very large excess. Now, since the theoretical quantity of soda required to neutralise the acid bodies, pectose and lignin, is only about 16 to 17 per cent, it is evident that the overhead method, with its consumption of 25 to 27 per cent is compelled to employ and to waste a considerable excess.

A second reason for the use of this excess is one also imposed by the defects of the method. It does, to some extent, check the pulp-staining by holding more thoroughly in solution the gelatinous pectoses. It is a common observation among paper-makers that the more soda used the less is the consumption of bleach.

The best results hitherto obtained by the older method have been round about 26 per cent of soda, calculated on the raw material weight and 16 per cent. of standard English bleaching powder, calculated on the unbleached pulp weight. These we have been able to reduce to 19 per cent and 11 per cent respectively, so chemical cost is now considerable below the best wood-pulp practice. Both sets of figures, for soda and bleach and for both methods, are subject to variations up or down of 1 to 2 per cent, in accordance with the slightly varying analysis of species. There is also a gain of 2 per cent in pulp yield in the fractional system, owing to its less drastic conditions of both digestion and bleaching, and a considerable saving in capital cost of the soda recovery plant. In the overhead system the wash liquors used in leaching out the spent soda from the digested pulp are staining liquors, and cannot be used again for digestion. They must go to the recovery plant, and as they are of low density they must be concentrated in an expensive multiple effect vacuum apparatus. As a result of the clean cut effected by the fractional method between the staining and the non-staining liquors the wash liquors can be used up in the chain of operations comprised in the regeneration of the recovered soda and the charging of the digesters. Only the digestion liquors need go to the recovery, and these are of sufficient

density to be dealt with by a comparatively inexpensive concentrating and calcining plant.

In factory practice it is not necessary to deal with the starch and pectose groups separately. They can be extracted together by a one to two per cent soda solution—the water deals with the former and the soda with the latter—and the liquor used for such combined separation is preferably that previously used for lignin digestion as long as it contains sufficient free soda to effect the purpose. In quantity this is equivalent, for bamboo, to from 6 to 7 per cent on the raw material weight. The high temperature lignin resolution should, therefore, be conducted with about 7 per cent more than is necessary for the lignin treatment, thus giving it the advantage of high density already alluded to and securing that the residual liquor from the operation shall contain sufficient free soda to effect the pectose resolution in a subsequent charge of raw material. Both operation are, therefore, conducted with one volume of liquor, with obvious advantage to the recovery process, and there is also exhibited that curious property of some colloidal solutions that they are more effective solvents of another colloid than pure solutions The pectose resolution may with advantage in hastening the process be conducted at temperatures higher than boiling, as long as these do not approach the point at which lignin begins to be affected. As this is somewhere about 130° C., we can safely go up to 120° C.

The figures given above are those resulting from the use of a "straight" soda liquor, that is, one manufactured from carbonate of soda, and of which the essential reagent is sodium hydroxide or caustic soda; but the modification known as the sulphate system is equally applicable to fractional treatment and with results corresponding comparatively for the two methods with those given above. With it the losses during the cycle of operations are replaced by crude sulphate of soda instead of carbonate, and the resulting digesting liquor contains caustic soda and sulphide of soda in the proportions of about three to one. For the overhead method it does possess advantages such as would compel us to use it were we tied to that system. These are:—

(*a*) The sulphide does more effectively deal with the gelatinous pectoses than caustic soda, and so to some extent checks pulp-staining.

(*b*) The sulphide checks to some extent hydrolysis of fibre at high temperatures by the caustic soda and so results in a slightly higher pulp yield.

Its disadvantages are:—

(*c*) Sulphide has little effect upon lignin, and to maintain the quantity of caustic soda necessary to deal with it the combined total of this and sulphide is 2 to 3 per cent more than is required with "straight" soda liquor.

(*d*) Crude sulphate of soda contains considerably less real alkali than the usual commercial form of carbonate, which is practically a pure article; consequently a larger quantity of the former must be imported at a high freight cost.

(*e*) The objectionable odour it evolves would rule it out in populous districts, though this will probably not apply in the localities suitable for bamboo pulping.

Since fractional digestion effectively gets rid of pectoses before the real digestion, that of lignin, begins, advantage (*a*) is cancelled out and advantage (*b*) considerably reduced in value by the lower temperature at which it is conducted, so the choice between the two is reduced to a question of the relative costs of the actual soda contents of sulphate *versus* carbonate of soda *plus* the 2 to 3 per cent alluded to in (*c*). Where freight cost is high the lower soda content of sulphate and the additional 2 to 3 per cent referred to may quite possibly leave the advantage with carbonate, notwithstanding the lower cost of the former at its poin of origin.

It will be evident from the above that our efforts have chiefly been along the line of soda treatment. Considering that bamboo is a grass exhibiting all the characteristic chemical constituents of grasses in general, and especially in the large content of unbleachable starch and pectous matter, it seemed to us that success was more certain along the lines held to be essential with grasses already in use, such as Esparto, and the other standard system of treatment extensively used for wood, known as the sulphite method, has never been seriously proposed for these. But this does not rule out entirely the application of the latter to bamboo, and simultaneously with our efforts an investigation on such lines has been going forward in this country, the digesting liquor being a bi-sulphite of magnesia. It is uncertain if it will result in lower costs than soda treatment, but it will probably succeed in producing a distinctive type of pulp, which will be all to the good of bamboo, as a whole, and reinforce its claims as an alternative to wood-pulp. The latter is produced in about equal quantities by both methods, and each is valued for its distinctive paper-making qualities.

The preparation of bamboo prior to digestion has given rise to some difference of opinion. It is somewhat noteworthy that such differences as exist relate entirely to the practical details of treatment. No difference exists as to the suitability of bamboo for the manufacture of papers requiring high bleaching and printing qualities. As regards preparatory treatment, two schools have arisen, the crushers and the chippers. Reduction to chips is the wood-pulp practice, and its advocates appear to be in danger of a wood-pulp obsession, which renders them somewhat blind to obvious differences between the two materials. They are undoubtedly entitled to make all the argument they can from the fact that crushing expands the volume of the material to nearly double, and, therefore, apparently reduces the capacity and output of the digestion to half that obtainable with chipped material. I say apparently, for the actual result is not quite so bad as that. By reason of its lesser resistance to liquor penetration, crushed material digests in three-fourths of the time required for chips, so if the output of a digester charged with chips is represented by 15, the output of one charged with crushed material is not 7½, but 10 Further, crushing does not create any additional recurring costs, but merely a greater capital outlay for the additional digesters required. Still, the objection is a valid one, and entitled to full consideration, but we think it is more than couterbalanced by what emerges from a critical study of the physical and constructional features of the two materials, thus:—

(*a*) The fibre bundles of bamboo lie perfectly

parallel to each other with no cross-graining and no interlacing; they split cleanly and crush perfectly without reducing to dust. Wood will not crush without a considerable loss through dust.

(*b*) Bamboo is thickly studded with groups of sap canals, which run perfectly parallel throughout the whole length of the stem. In the dry material these are filled with air, which, being in a state of capillarity, is extremely difficult to dislodge, and, in the case of chips, offers a powerful resistance to the penetration of liquor, besides adding to the buoyancy of the mass and tending to float a portion of it above the liquor. The splitting, which is the first effect of crushing, runs along these canals, which are thus laid open to attack by liquor on their interior surfaces and the capillary air is got rid of. Wood presents no such feature.

(*c*) Baboo, throughout the entire length of stem, is of homogenous one-aged, one-season growth. Wood, if say, 60 years of age, has its heart wood 60 years old, while its outer ring of growth is one year old. Therefore it must contain differences in density and quality, and, consequently there must be a proportion of undigested chips in wood-pulp digestion. There is no need for such a must in the case of bamboo.

(*d*) The nodes of bamboo, contrary to general belief, are not denser than the internodes. Their specific gravity is about 5 per cent less. But they contain more pectose and lignin and their colloidal resistance to liquor penetration is, therefore, greater. The antidote to this is opening up their tissues completely. By crushing, this can be done so thoroughly that they can scarcely be distinguished in the general mass. As chips they must result in a considerable proportion of undigested specks and blemishes in the pulp.

The chipping school, under the influence of their wood practice obsession, are quite reconciled to the presence of this undigested matter in their pulp. They regard it as natural and expend their energies upon means of screening it out of the pulp after it is cooked. The crushers say it ought not to be there at all, that there need be no undigested chips in the pulp except occasional accidentals, due to particles of raw material getting lodged over rivets or otherwise hung up in the upper part of the digester beyond the reach of liquor, and they think this is a result well worth attaining at the cost of somewhat larger digester plant; and they claim further that since crushed material will digest with less drastic conditions of time, temperature and soda, the digestion cost is less and the pulp yield more.

(To be continued).

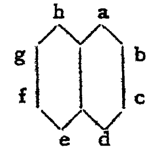
## THE RATIONAL NOMENCLATURE OF THE NAPHTHOL, NAPHTHYLAMINE, AND AMINO-NAPHTHOL SULPHONIC ACIDS.

By E. de BARRY BARNETT, B.Sc., F.I.C.

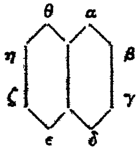
THE importance of the naphthol, naphthylamine, and amino-naphthol sulphonic acids in industry has lead to their being given trivial names. Unfortunately, these names give no clue as to the orientation of the groups present, and are very confusing, as some acids have received as many as three different names, whereas in other cases the same name is used to denote quite different acids. Thus, Cain in "The Manufacture of Intermediate Products for Dyes" (1918), describes two different acids as F-acid, and no less than four different compounds as S-acid. Further, if different authorities are consulted it will often be found that they use different names for one and the same substance.

In order to avoid confusion, the present writer, several years ago, devised a system of nomenclature for his own use which has the advantages of being simple, definite, and at the same time indicating the orientation of the groups present in the molecule. The method has proved to be so useful that it may be of interest to other chemists who have to deal with intermediate products. It may be briefly described as follows.

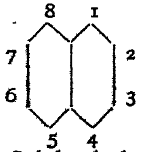
Each of he eight positions in the naphthalene ring system is denoted by (1) a letter of the English alphabet; (2) a letter of the Greek alphabet; and (3) a numeral. These positions are shown in the accompanying diagrams. The use of letters of the English alphabet is reserved exclusively for denoting the positions of amino-groups, hydroxyl groups being invariably denoted by Greek letters, and sulphonic acid groups by numerals. The words "amino," "hydroxy," "sulphonic," and



Amino groups



Hydroxyl groups



Sulphonic Acid groups.

"naphthalene" being superfluous, are omitted in building up the names. The following three examples serve to illustrate the method.

2-Aminonaphthalene-6-sulphonic acid (Brönner's Acid) becomes b.6 acid. 1-Naphthol-4-sulphonic acid (Nevil and Winther's Acid) becomes α.4 acid. 1 : 8-Aminonaphthol-3 : 6-disulphonic acid (H-acid) becomes α.h.3.6 acid., or a.θ.3.6 acid. It will be noted that all the names are short and that the positions of the groups are indicated definitely. The names have been found particularly useful in denoting the structure of the azo-dyes.

It may be urged that the Greek letter "zeta" (ζ) is inconvenient to write. This is true, but it will be found in practice that it is very rarely, if ever wanted.

For the very common acids such as naphthionic acid, R-acid, NW-acid, &c., colour chemists will probably prefer to retain the present names, but for the acids less frequently encountered the above system will be found to be very convenient.

## UNIVERSITIES, RESEARCH, AND BRAIN WASTE.*

By J. C. FIELDS, Ph.D., F.R.S.

*To the Members of the Royal Canadian Institute.*

IT is my desire, first of all to thank you for the honour which you have conferred on me by electing me your President for the year now beginning. The two past years have been prosperous ones

*Reprinted from the *Transactions of the Royal Canadian Institute*, February, 1921.

under the Presidency of Dr. J. Murray Clark. Many new members have joined and the attendance at the meetings has appreciably increased. The Institute has carried on its propaganda for research both in regard to its application to industry and on the purely scientific side. In its campaign it has been aided by a succession of eminent lecturers from the United States. The activities of the Institute will continue to be directed by the same policy as hitherto, and I may say that arrangements have been made for a group of exceptionally able men to lecture under its auspices in Toronto during the coming winter.

With your permission I shall now turn my attention to the consideration of the subject which I have selected for my address this evening—"Universities, Research, and Brain Waste."

Whatever the undeveloped resources of a country may be, the greatest of all its resources is the brain of the people, and more especially the brain of the exceptionally gifted. Other resources in fact are made available only by combination with this primary resource. The wealth of the race consists of the thoughts of a limited number of men accumulated through the generations. By means of these thoughts, or certain of them, we are able to reproduce things. It takes no great mental effort to realise that of all the material products of man's hands which existed 50 years ago, that which persists to-day is negligible.

There exists a body of men whose function it is to increase the wealth of the race, to add new thoughts to the fund already accumulated. These are the so-called research workers. Men or research inclination there have been in all countries and in all periods. In recent times, however, the number has increased greatly. Certain universities in America, and a large proportion of those in Europe, regard it as one of their functions to prepare men to do research. Many of the European universities regard it as their chief function.

The research workers are makers of modern history as no other body of men are. The difference between the conditions under which our forefathers lived 300 years ago and those under which we live to-day is due to the research workers. The layman little realises what an influence individual men among these research workers exercise upon his daily life. In ordinary conversation the name of Shakespeare is heard more frequently than that of Newton, and students of the great dramatist will be surprised to be told that Shakespeare as a factor in determining their lives is a bagatelle compared to Newton. The thought of the great scientist, as a matter of fact, permeates our civilisation, and can be traced distinctly in a multitude of conditions which surround our every-day life. To justify our statement, it suffices to refer briefly to Newton's discoveries of the calculus and the law of gravitation. The calculus is the basis of the greater part of higher mathematical analysis. It is the most powerful of all instruments in handling geometrical problems, and it has opened up new territories in geometry which are all its own. What I want more particularly here to refer to, however, is the role which the calculus plays in connection with physical phenomena. Its aid is invoked in questions which relate to motion, light, heat, electricity. The principles of dynamics are formulated in terms of its notation. Unfortunately it has had a share in the development of modern artillery, for the theory of projectiles is an application of the calculus to the law of gravitation. It has had its place in the advances which have brought us the electric light, the trolley, the power house, telegraphy, and telephony, both with and without wire. When we read the despatches and cablegrams in our morning paper we do not pause to remind ourselves that the thought of Newton is one of the factors which has made this possible. No more does it occur to the baseball enthusiast that he is under any debt to Newton when he stands before the newspaper office down town and scans the latest baseball bulletin.

Transportation by sea, by land, and by air, has much for which to thank Newton. The calculus had nothing to do with the invention of the steam engine by James Watt. It has, however, done important service during the last half-century or more in handling problems relating to steam engines and turbines where fundamental principles have been involved. It has had its effect on naval construction. It is involved in the general question of the relation between shape, power, and speed in connection with a vessel. It is essential to the study of the strains and stresses in a ship's members. Navigation, too, depends on astronomical data, the obtaining of which involves the use of the calculus. Our clocks and watches are regulated by data so obtained. It has had its share in the development of the automobile engine. It proves itself useful in problems connected with hydraulic elevators. It played a fundamental role in solving the initial difficulties connected with flight, and later on it was an essential instrument in solving the problem of stability in relation to aeroplanes. It renders valuable assistance in connection with the finding of necessary data for the putting up of large steel bridges and for erecting other engineering structures. Physical chemistry makes extensive use of the formulæ of the calculus. The physiologist, too, when he is confronted with problems in surface tension is forced to call in its aid.

The same god-like instrument enables the astronomer to follow the earth and the planets in their courses about the sun and to keep track of the moon in its more devious path around the earth as the latter whirls about the sun. It renders it possible for him to measure the combined and varying tugs of the sun and moon on the waters of the earth, and with its formulæ he traces the paths of the particles of water that go to make up the tides as they travel across the oceans of the earth. By the aid of this instrument applied to the solar system, on the assumption that it is regulated by the law of gravitation, Adams and Leverrier, led thereto by certain inequalities noted in the motion of the planet Uranus, deduced the existence and location of the planet Neptune and foretold its mass and orbit.

Clerk Maxwell it was who formulated the theory of electricity and magnetism in terms of the calculus. Hertz devised the experiment which verified the existence of certain waves in the ether predicted by Maxwell from his theory, and Marconi utilised these waves for wireless telegraphy. In later times, we have become familiar with X-rays, radio-activity, and the theory of electrons. The physicist studies the relative positions of the atoms in a molecule and going beyond distributes

he atom itself into electrons. He tells us wonlerful stories about the energy locked up in an ıtom, and Sir Oliver Lodge informs us that if his atomic energy were only available, a ton of natter day by day would suffice to supply the ıeeds of Great Britain. Going over from the inınitely small to the infinitely great, that eminent Dutch astronomer and hardy generaliser, Kapeyn, has launched a scheme to study the strucure of the universe. His nearest material is over :5 trillion miles away, but his scheme is under vay, and he is steaidly accumulating his data. At some stage in the development of all the 'ranches of physical science here referred to, Newton's thought has played a role and the cal:ulus has proved itself a helpful intrument in egions undreamed of by its discoverer.

In what precedes I have touched on the physical ciences and the application of the calculus to hem. I have mentioned but a few among the nany great names associated with the develop-nent of these sciences. I have wished in a few words to do the impossible, to suggest to the lay-nan by an illustration something of the reach and mportance of research, to indicate how the work of one research man connects up with that of another, and to shadow forth how intimately the ife work of some great thinker may be related to our daily life and activities without our being conscious of the fact. Newton himself, it may be pointed out, was not such an unconditioned being that his work was independent of that of the workers who preceded him. The discovery of the calculus was already a foregone conclusion after Descartes had invented analytical geometry. In the hands of a lesser genius, however, its scope would not have been as fully appreciated, and immediate results would have been more meagre. I wish that I could convey briefly to the laymen in my audience some conception of the nature of the calculus, but this is not within my power to do. That will, perhaps, not be surprising in view of the fact that a hundred lectures are devoted to introducing the honours students in mathematics and physics to the subject in their second year, and that a considerable portion of their time in their third and fourth years is utilised in increasing their appreciation of its scope and application.

In the foregoing I have said nothing about the immense contributions of chemistry to the health, wealth, and comfort of mankind. I have not referred to the debt we owe to biology, botany, bacteriology, geology, and varous other branches of science. I have pointed out the successive dependence of one man's work on another's. I would draw attention also to the simultaneous co-operative character of scientific work. For hundreds of research workers in different parts of the world are at the same time busied on the same problems or on related problems. They keep in touch with one another's work principally through highly specialised journals which the layman never sees. In these journals as a rule the results of their investigations are published. To expedite matters it has been found necessary to devise certain aids. One of these is the International Catalogue of Scientific Literature which, before the war, appeared annually in 17 volumes, each volume corresponding to a separate branch of science. Besides an alphabetical list of authors each volume contains an elaborately classified subject index. This, however, in view of the mass of material being turned out, does not suffice for the needs of the research worker who wants speedy orientation with regard to everything which may have a bearing on his own special line of work. For this something more than a mere classification of titles is needed. Some further indication as to the contents of an article is necessary. The need here referred to is more or less satisfactorily cared for in different branches of science. In physics and electrical engineering, for example, we have what are called "Science Abstracts."

The need of orientation will be better realised by the layman when he is told that the number of titles listed in the 17 volumes of the International Catalogue for the year 1912 was 67,926. The great bulk of the literature here referred to is of research character, and its authors number up in the tens of thousands. The individuals in this army of investigators vary greatly in ability. Many of them are handicapped by the conditions under which they have to work. The products of their efforts are, of course, very unequal. In the aggregate, however, the importance of the activities of the army of research workers to the welfare of the nations can hardly be overestimated. How many of the nations—how many of the individuals who go to make up the nations—realise this fact? How many of our own people appreciate it adeuately?

*That does not exist which I do not see* is the most prevalent and most disastrous of all fallacies. Every day men in high places act on this fallacy. It shapes important policies and determines great issues. It came very near being the undoing of Great Britain when the opening of the war found her scientifically unprepared, for her statesmen in taking counsel had been accustomed to leaving out of account science which, as it proved, was the most important factor in the situation. It is my own conviction and that of all scientists with whom I have discussed the matter that the modern research movement is the greatest intellectual movement in the history of of the human race. How many Governments act as if this conviction had taken hold on them? In how many of the universities on this continent have those in authority seen the vision?

The natural home of research is in the universities. There most of the fundamental discoveries in science have been made in the recent past. Let us hope that this may continue to be the case in the future. The highest functions of a university are on the one hand to provide place and opportunity for the research worker to carry on and make his discoveries and on the other hand to train young men of selected ability to use their creative faculties. This is more fully appreciated in certain European countries than in America.

In Germany, at least before the war, no man was appointed to a university staff who had not proved himself to be intellectually productive. Once appointed, he could lecture as little or as much as he pleased. He could devote practically all his time to research if he was so inclined. He was relieved of financial worry. He did not need to preoccupy himself with what, under certain eventutlities, would become of his wife and

family. Everything was provided for in advance, so that, with a mind at ease, he could concentrate all his powers on his science. On the instructional side the German university had particularly in mind the student of exceptional ability. It put no obstacle in the way of admitting others. It was not a difficult matter to obtain a degree. The arrangements, however, were made with a view to the needs of the more highly gifted. These were trained to be research workers, and those who distinguished themselves most in research received preferment later on. The intellectually productive men then enjoyed a certain prestige in Germany before the war. This was overshadowed, however, by the factitious prestige attached to the military uniform, and we know how the war-mad militarists of Potsdam prostituted German science and purposed by its aid to subjugate the rest of the world.

In France, perhaps more than in any other country, is intellectual achievement honoured. An intellectual aristocracy, according to Prof. Le Chatelier, is essential to the French democracy. This means that intellect is trained to the service of the State. In peace times membership in one of the five academies which constitute the Institut de France, a purely intellectual distinction, is the highest honour to which a Frenchman can aspire. The Institut, it may be noted, through its academies, disposes of considerable sums as rewards for notable intellectual achievements. The Academie des Sciences in particular has a long list of prizes which are awarded from time to time to scientists who have solved specified problems or have made advances along certain lines in Science. Living, the creative thinker is regarded as the glory of his country. When he departs this life his remains are buried in the Pantheon with funeral rites which vie with those accorded to a President of the Republic.

(To be continued).

## PROCEEDINGS OF SOCIETIES.

### GEOLOGICAL SOCIETY.

*June* 8, 1921.

MR. R. D. OLDHAM, F.R.S., President, in the Chair.

A DISCUSSION on the "*Relations of the Northern Red Sea and its Associated Gulf-Areas to the 'Rift' Theory*" was opened by Dr. WILLIAM FRASER HUME, in the following words:—

(1) The areas specially considered are the northern portion of the Red Sea and a region to which the name of "Clysmic Gulf" has been given. The Clysmic Gulf (from Clysma, the Roman name for Suez) is defined as the district bordering the Gulf, and lying between the (largely) fault-bounded ranges of Egypt and Sinai on the west and the east respectively which dominate this depressed area. Within its borders Miocene deposits are of wide distribution; beyond them, these are notably absent. The folds within this region are from north-west to south-east, outside it their their trend is frequently almost at right angles.

(2) A line prolonging the direction of the western coast of the Gulf of Akaba to the shores of Egypt divides the Clysmic Gulf from the Red Sea, the former being occupied by the shallow Gulf of Suez and disturbed lowlands, while south-east of the dividing-line is the Red Sea, with its great depths and its narrow coast-line.

(3) The Clysmic-Gulf area is one of complicated fold-and-fracture effects, while in that of the Red Sea only fold effects have been observed.

From a study of the facts known, it is concluded that.—

(4) The whole region under consideration underwent extremely slow submergence, the negative movements continuing from early Jurassic to late Cretaceous times.

(5) This was succeeded by one of a positive nature, the actual emergence of the new land taking place near the close of the Eocene Period. It is suggested that the area was occupied by an anticline or anticlinorium plunging northwards in the Clysmic Gulf region, and that it was subject first to marine and then to subaërial erosion. This formed part of the continent on which grew the trees of the Petrified Forest, and on which wandered animals such as the *Arsinoitherium* and the earliest elephants. This continental period was most marked during the late Eocene and early Miocene times, and the area dealt with here appears to have become one of very varied ridge and depression.

(6) The whole region thus dissected was invaded by the ancient Mediterranean; the slow advance southwards occupied the main portion of the Miocene Period, and probably extended well into the Pliocene. The pre-existing ridges became coral-reef centres: the intervening depressions were filled up, first by land-derived deposits (such as conglomerates and clays), and then by lagoon formations (gypsum and salt). The earliest of these formations appear to have been of Schlier (Middle Miocene) age.

(7) The sequence of events from Middle Pliocene times onwards is difficult to unravel. The whole region of the Clysmic Gulf became folded and fractured to a remarkable extent, there being certain underlying elements of order discernible. There is strong faulting at the borders with the igneous hills, and fold-ranges are well marked, these being of a symmetrical anticline type. It is suggested that compression of the area, with uplift of portions of it, offers the best solution for the facts observed. It seems difficult to conceive that dislocation so marked, spread over so wide an area, could arise under rift formation as defined by Prof. J. W. Gregory. It seems equally difficult to ascribe the whole of the surface-differences to erosion alone. It will be readily understool that no simple solution of the problem can be offered on the evidence at present available, especially in view of the fact that no important faulting has been noted on the western borders of the Red Sea.

(8) The same reserve must be exercised with regard to the very interesting eroded trough-fault valleys, which the writer formerly regarded as of rift origin.

(9) A suggestion is made that the portion of the Nile Valley about lat. 26° N., where faulting is most conspicuous, may have been initiated by erosion of a sharp anticlinal fold due to the compression of almost horizontal strata. Sharp

folds exist in the desert east of the Nile, but their origin is at present doubtful.

DISCUSSION.

The PRESIDENT said that it had been customary of late years to devote at least one meeting in the session to a lecture on some subject of interest to geologists, or to a discussion of one of the larger and more speculative problems of geology. The subject selected for discussion that evening might be briefly defined: there was in Central Africa a well-known surface-feature, for which Prof. J. W. Gregory had popularised the name of the Great Rift Valley; there was also, in Southern Syria, a similar surface-feature, occupied in its northern part by the Jordan Valley, and continued as a surface-depression to the Gulf of Akaba. According to one school of thought, these two surface-features were not only of similar genesis, but formed the extremities of a continuous surface-feature, intimately related in origin to the tectonics of the surface-rocks, called the African Rift Valley, of which the Red Sea was regarded as an integral and important section. According to another school, no such continuity is recognised, and the origin of the Red Sea is attributed to causes other than those which gave rise to the rift-valleys of Africa proper and of Palestine. Dr. Hume had had a large personal experience of the geology of the Red Sea region, and his presence in England afforded a useful opportunity of raising a discussion of this important and interesting problem.

Col. H. G. LYONS expressed his great interest in the information that Dr. Hume had laid before the Society, which made the structure of this part of North-Eastern Africa much clearer. He agreed that former assumptions of the rift character of the Nile Valley were not tenable, and that the Gulf of Suez, too, could not be strictly described as a rift-valley. For the Red Sea, he asked whether more information had been collected of late as to the structure of the eastern shore, to show whether it was as free from fracture-lines as the western was, according to Dr. Hume's account.

Prof. J. W. GREGORY, in a letter sent as a contribution to the discussion, remarked that the agreements between Dr. Hume's views and his own were more essential than the differences. The sequence of events stated by Dr. Hume for the Clysmic Gulf is similar to that which he had adopted for the Rift Valley as a whole—including Jurassic subsidences due to the Mesozoic deformation of the crust, an Eocene land over the Red Sea, subsidence of the Rift-Valley trough in the Oligocene, renewed and extended especially in the late Pliocene Period. The Gulf of Suez is not typical of the Rift Valley, as its lines there intersect those of the Levant, and as the rocks traversed are mostly young stratified deposits.

The main difference between the writer's interpretation and that stated by Dr. Hume is the relative importance of fold and fault. The importance of the faults is indicated by Dr. Hume's remark that "the (largely) fault-bounded ranges dominate this depressed area," and by his statements (*Geol. Mag.*, 1910) regarding the dome over the Clysmic Gulf: "I can conceive of no erosive agent which would break across this great earth-feature without the intervention of fracture [and that] "faulting, and faulting alone, can explain the phenomena." These conclusions are supported by the recent statements in bulletins by the Geological Survey of Egypt that faulting was "the controlling factor in the formation of the shore line of the Gulf" [and in] "determining the present position of the Gulf of Suez."

The attribution of the Red-Sea section of the Rift Valley to folds appears to be due to the use of the term "fold" for movements which the writer regards as faults. The Geological Survey of Egypt has recently explained its use of the word "fold" by a diagram (*Petrol Res. Bull. No.* 6, 1920, sketch before p. 1) which identifies a steep, plane, slickensided surface as a fold. The writer regards the movement shown by this diagram as a fault, so that the difference is a question of terms. He found it impossible, in view of the post-Eocene faults with fault-breccias beside the Gulf of Aden and the maps of the Egyptian Geological Survey at the other end of the Red Sea, to accept the view that that on the Red Sea only fold-effects have been observed. He agreed that the Lower Nile Valley is not a Rift Valley, its structure being the antithesis to that of the Red-Sea trough.

With regard to the length of the Rift Valley, he referred to the explanation in his forthcoming book, "The Rift-Valleys and Geology of East Africa" briefly stated in *Geogr. Journ.*, lvi., 38), representing it as due to world-wide mid-Kainozoic earth-movements, and to its position between the mountain-forming movements in Europe and Africa which were northward, and the simultaneous Asiatic movements which were southward. Its great length is due to the continental scale of the accompanying movements, and seems no more inconsistent with its formation by tension than the equal length of the contemporary fold-mountain system is inconsistent with their formation by compression.

Dr. J. W. EVANS thought that the structure of the Akaba and Clysmic gulfs would prove very different, the latter being probably the same as that of the Dead-Sea depression. He enquired whether the faults shown in Dr. Blanckenhorn's map near Suakim, parallel to the coast in that neighbourhood, and approximately parallel to the Gulf of Akaba (though not in the same line), were authentic, and, if so, whether they had a downthrow towards the sea. The deep depression in the north of the Red Sea was sharply defined, both on the north and on the south, and suggested a subsidence. The existence of a "graben" seemed to point to a state of tension, when it was found, but did not imply the existence of a rift as wide as a sunken area. The speaker looked forward to the production by the Egyptian Survey of further evidence on this most important question.

Mr. G. W. LAMPLUGH remarked that the "rift-valley hypothesis raised the wider question as to the supposed prevalence in many parts of the world of large-scale surface-features produced directly by comparatively recent faulting. The geological record showed that the local development of troughs of depresession had been frequent throughout the accumulation of the stratified rocks; and the resultant synclines were often faulted longitudinally at the margins, as well as within. But the field-evidence generally implied that the subsidences had been gradual, and the faults of slow growth. Secondary "fault-controlled" features, due to selective denudation, were common enough both in valleys and on high

ground, but new orginal fault-scarps were difficult to find; he had not yet himself seen a single convincing example, though he had seen several to which this origin was ascribed. He knew no case of the trunk-drainage of a land-area having been revolutionised by the uprise of a fault-block athwart it; and this seemed to imply that the surface-effects of faults for a long time past had never been rapid enough to overcome the ordinary course of weathering and erosion. The conception of the "rift-valley" had always been attractively simple, and there may be features on the earth to which the conception will apply absolutely; but the researches of Dr. Hume and his colleagues have shown that we must now look elsewhere than in Egypt.

The PRESIDENT said that the interesting and instructive discussion had left two doubts in his mind still unsatisfied. One was whether two distinct problems, the origin of rift-valleys and the origin of the Red-Sea depression, had not been confused. The magnitude of the Red-Sea depression was of so different an order from that of the African rift-valleys, that any similar rifting, which may have taken place, would be of subsidiary importance in determining the position and form of the Red Sea. The other doubt was as to the existence of anything which could properly be called the Great Rift-Valley. There was in Africa a belt of country in which the surface-form known as a "rift-valley" was of fairly frequent occurrence; but it seemed to him that there was insufficient evidence of continuity between them, or of the existence of one continuous rift-valley. It appeared more likely that further investigation would prove the independence of the individual depressions, which should rather be regarded as separate members of a continuous range or series.

Dr. W. F. HUME, in reply, thanked Col. Lyons for his remarks, and pointed out that Dr. Blanckenhorn had never himself visited the Red-Sea region, the faults inserted having no basis of observation. With regret it had to be stated that Dr. Blanchenhorn was frequently incorrect in regard to the existence of faults in Egypt. He had bordered the Fayûm with faults and then removed them, shown an important one at Moghara Oasis which could not be confirmed, and finally bordered the Red Sea with faults where proof of their existence was absolutely wanting.

Prof. Gregory was certainly justified in stating that the actual diagram exhibited was a true fault; but, if continued, it passed into a monoclinal fold. The point did not affect the main issue, as the section was within the area of admitted fracture.

Instead of assuming all the depressions discussed as part of a great Rift system, each had to be considered on its merits. The parallelism of the Red-Sea borders could be explained as due to erosion of a broad fold, and, apart from the apparent absence of faulting on the large scale along its borders, the breadth of that sea was such as to make it most difficult to conceive it as a tension-crack. In the Clysmic-Gulf area, which was narrower, and lying between hill-masses of granite or limestones, folding and fracture were intensely marked, but might well be due to compression. The features on which special attention would have to be concentrated in connection with rift questions were the relatively narrow valleys of the Jordan, the Dead-Sea depression, and those of South-Eastern Sinai, for which no simple erosion theory seemed satisfactory. They were undoubtedly, like the Clysmic Gulf, fault-guided or fault-controlled depressions. The speaker, as a result of his own studies, agreed with Mr. Lamplugh that a dogmatic assertion of rifts at this stage might give a bias to younger geologists which might cloud the truth, this being one of Dr. John Ball's objections to Prof. Gregorys' original paper.

Dr. Hume also was glad to note the President's remarks, and thought the idea of "tension regions," as advocated by Dr. Evans on this occasion, was one to be approached with great caution, as it required very full experimental evidence.

## CORRESPONDENCE.

### QUATERNIAN SERIES* AND ISOTOPES.

*To the Editor of the Chemical News.*

SIR,—In considering the new individual atomic weights involved by reason of isotopes, it is of possible interest to examine some of the earlier speculations to see whether any symmetrical relations are possible. To this end (more as an illustration as to the importance of reviewing past work) the following scheme may be taken as an example. The readers of this Journal will, no doubt, remember my many attempts to work out the individual values for isotopes—these efforts dating back to 1914.

Making use of some of these values, and introducing Aston's experimental values for isotopes in heavy-face type, the arrangements here shown explain themselves.

The original scheme was:—

| | At wt. | Differences. | |
|---|---|---|---|
| Ar= | 39·9 | | |
| | | −16 | |
| Fe= | 59·9 | | −8 |
| | | −24 | |
| Br= | 79·9 | | −4 |
| | | −28 | |
| Ag= | 107·9 | | |

Considering isotopes, the scheme becomes:—

| | Lower mass isotope. | | | Higher mass isotope | | | |
|---|---|---|---|---|---|---|---|
| Ar= | **36** | | | **40** | | | |
| | | 18 | | | 16 | | |
| Fe= | 54 | | 7 | 56 | | 9 | (7+9=16) |
| | | 25 | | | 25 | | |
| Br= | **79** | | 3 | **81** | | 5 | (3+5= 8) |
| | | 28 | | | 30 | | |
| Ag= | 107 | | | 111 | | | |
| | | 71 (or 107-36) | | | 71 (or 11-40) | | |

It is of interest to note that Aston has succeeded in determining the isotopes of nickel, the values being 58 and 60 (see *Nature*, June 23, 1921). This, of course, has no direct bearing on the above, except to strengthen the strong tendency of isotopes to occur in pairs, *i.e.*, as regards species.

Schemes of the kind herein shown must be regarded as uncertain, since surprises are generally in store; but, so far as can be judged, the argon values seem to fit in very well with the others, though the difference between the mass values in this case is *four* units instead of *two*, as in the case of bromine.—I am, &c.,

F. H. LORING.

*See CHEMICAL NEWS, 1909, c, p. 37.

## ETHYLSTANNIC ACID.

*To the Editor of the Chemical News.*

SIR,—In the May issue of the *Journal of the Chemical Society* there appears an interesting paper by Mr. J. G. F. Druce, dealing with a newly-discovered acid having a formula $C_2H_5O.SnO.OH$. In the course of this paper reasons are adduced for regarding the substance as a compound of *stannous* tin; but apparently the author fails to be convinced by his own arguments, since he names the substance "ethylstannic acid."

The contention that "a rose by any other name would smell as sweet" sometimes put forward in excuse for a lax terminology, is, to my mind, very misleading. Exact and precise ideas need for their expression terms equally exact and precise, and it is with the development of such ideas, surely, that science is concerned.—I am, &c.,

H. STANLEY REDGROVE, B.Sc., F.C.S.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences.* Vol. clxxii., No. 26.

"Photographs of the Planet Venus."—By M. F. Quénisset.

"Action of Boric Acid on Glycerol and Polyvalent Alcohols. Application of a new Physico-chemical Method."—By M. René Dubrisay.

"Ammoniacal Silver Carbonate."—By MM. Dervin and Olmer.

"The Parts played by Gaseous Impurities in the Catalytic Oxidation of Ammonia."—By M. Eugéne Decarrière.

"Influence of Forging on the Toughness of Steel."—By M. Eugéne-L. Dupuy.

## NOTES.

BOARD OF TRADE ANNOUNCEMENT.—The Board of Trade announce that by an Agreement made with the German Clearing Office, now awaiting the approval of the Reichstag, the time for lodging claims with the British and German Clearing Offices by their respective nationals under Article 296, Section III., Part X., of the Treaty of Versailles, has been extended to September 30, 1921. No further claims under the above Article will be accepted after that date by the Clearing Offices concerned.

AN announcement has been made to the Académie des Sciences by Baron Edmond de Rothschild of his intention to devote the sum of 10 million francs to the foundation of a laboratory of scientific research, to be chiefly devoted to the development of physical and chemical science.

THE British Cast Iron Research Association has obtained a licence under Section 20 of the Companies' (Consolidation) Act, 1908. *President*—The Right Hon. Lord Weir of Eastwood, P.C., D.L., LL.D. (Glasgow). *Secretary* — Thomas Vickers, Central House, New Street, Birmingham. We have a pamphlet giving particulars of the Association, together with the objects and the history of the movement, and inviting application for membership. The cast iron industry is of great national importance, as nearly every other industry in the country uses its products. It should, therefore, possess the strongest and most progressive Research Association in the country. With the support which its importance deserves, this should be readily accomplished. Every individual firm engaged in the production of cast iron should consider that it is to their vital interest that the Association should have their practical support, because the result of its work must necessarily mean that the foundries who are members will be in a position to deal with foreign or any competition on better terms than at present by the reduction in cost of manufacture, by impovements in the quality of castings, and the output should be greatly increased by the simplification of processes and the analysis of materials used.

MANUFACTURE OF SUPERPHOSPHATES. — H.M. Charge d'Affaires at Montevideo reports to the Department of Overseas Trade that by a Bill recently sanctioned by the Chambers, the Institute of Industrial Chemistry is authorised to expend the sum of $60,000 on the construction and installation of a factory of calcium superphosphates, and the extension of the sulphuric acid plant. A yearly expenditure of $1,000 for a period of three years is also authorised for purposes of propaganda, and experiments with superphosphates as fertilisers. On the promulgation of the law in question the exportation of bones, &c., will be subject to a duty of $8 per 1000 kilogrms., and should necessity arise, the exportation of such articles may be prohibited.

WE have received a copy of *Le Verre*, Revue Mensuelle des Industries et du Commerce due Verre. The paper, under the direction of A. O. E. Gobbie, contains all information connected with the glass industry in Belgium. The London publishers are Messrs. Gordon & Gotch, Ltd., 15, St. Bride Street, E.C.

AN announcement has recently been made that the following French radio engineers have been nominated Chevaliers of the Legion of Honour for their inventions: J. Bethenod (high-frequency alternators); E. Bloch (applications of vacuum tubes to radiotelegraphy); L. Bloch (applications of vacuum tubes to radiotelegraphy).

FOR the first time, so far as is known, wireless telephony has been used to transmit services from one church to another in order that a congregation without a regular pastor could have the benefits of Sunday evening worship. The churches involved in this test were the Calvary Episcopal and the Herron Avenue Presbyterian, both of Pittsburg, Pennsylvania, U.S.A., and for several months past the Sunday evening services of the former church have been broadcasted by radio from a test station in East Pittsburg. The arrangements were made by the Westinghouse Electric & Manufacturing Co. For reception, a loop antenna, amplifier, and condenser, was placed on the rostrum in front of the pulpit. The loud speaking horn rested directly on the pulpit. The music, singing, and sermon were clearly received in the second church.—*Radio Review*, July, 1921.

Contribution to the Study of the Acid Constituents of the Resin of the Maritime Pine. Isomerisation of the Pimaric Acids.—M. G. Dupont.—Abietic acid, the chief constituent of various resins, is not a pure body, but a complex mixture of isomorphous acids only one pure constituent of which has been hitherto separated, by Schultz. These acids not existing in the resin, but being the result of isomerisation by heat of the pimaric and sapinic acids, it is logical to endeavour to obtain pure abietic acids from their mother acids. In a previous paper, M. Dupont explained how he decomposed pimaric acid into its two constituents, dextropimaric acid and levopimaric acid. In this note he studies the products of isomerisation of this latter acid.—*Comptes Rendus*, May 30, 1921.

Palm Oil for Motor Cars.—Experiments have made with a view to substituting palm oil for mineral oil in the French colonies, for internal combustion engines. These trials were very conclusive although fouling of the engines was to be feared. The motor was started with mineral oil, and when sufficiently heated, palm oil was substituted. This new fuel may have great influence on the utilisation of the soil in colonies where there is no mineral fuel. The calorific power of palm oil is 9228 calories.—*Industrie Chimique*, May, 1921.

Phenylurethanes of Terpenic Alcohols.—According to Mr. Weehuizen, it is advisable, when preparing phenylurethanes of terpenic alcohols, to employ as agent of dilution boiling petroleum, at 170° to 200° C., and work during boiling. Phenylurethane crystallises in cooling. He thus prepared borneol phenylurethanes, fusion point 137°—138° C.; menthol, fusion point, 111°—112° C. The same method was applied to eugenol and thymol. With a mixture of camphor and borneol the latter is well separated in form of phenylurethane.—*Industrie Chimique*, June, 1921.

## NEW COMPANIES.

The under-mentioned particulars of New Companies recently registered are taken from the Daily Register compiled by Jordan & Sons, Limited, Company Registration Agents, Chancery Lane, W.C.2.

Union Oils & Bitumen Co., Limited.—(174521)—Registered 27th June, 1921. Reliance Works, George Street, Smethwick, Staffs. To carry on the business of Manufacturers of Bitumen, Paints, Varnishes, Tar Products and Chemical Compositions, also Refiners and Blenders of Oils. Nominal Capital: £2,000 in 2,000 Shares of £1 each. Directors: G. H. Shakespeare, Oakhurst, 56, Lodge Road, West Bromwich; W. F. Edge, 17, Westbourne Road, Edgbaston, Birmingham. Qualification of Directors £100. Remuneration of Directors: £25 each.

Crusader Reviver Company, Limited.—(175500)—Registered 1st, July, 1921. Langham Place, Northampton. To acquire and carry on the business of Manufacturers of Inks, Stains, Dyes and Preparations for Polishing. Nominal Capital: £1,000 in 1,000 Shares of £1 each. Directors: W. L. Simmons, 135, St Andrews Road, Northampton; R. Barratt, 11, Birchfield Road, Northampton; G. Pragnell, 134, St. Andrews Road, Northampton; W. H. Henton, 30, Stimpson Avenue, Northampton; C. D. Henry, 22, Bostock Avenue, Northampton. Qualification of Directors: 100 Shares. Remuneration of Directors. To be voted by Company.

Babette, Limited.—(175497)—Registered 1st July, 1921. To carry on the business of Manufacturers of Toilet Creams and other Preparations. Nominal Capital: £300 in 12,000 Shares of 6d. each. Directors: To be appointed by Subscribers. Qualification of Directors: 1 Share. Remuneration of Directors: To be voted by Company. Subscribers: E. J. Burrows, 29, Lyndhurst Road, Highams Park, Chingford, E.4.; S. Humphreys, 19, Richmond Road, East Finchley, N.2.

## New Patents.

This List is specially compiled for the *Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, W.C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

17058—Barton, G. V.—Apparatus for manufacture of lead oxide. June 22.

16526—Wolfes, O.—Process for preparation of Tropinone-mono-carboxylic acid esters. June 15.

16248—Officine Elettrochimiche Dr. Rossi.—Drying or eliminating water vapours and nitric or nitrous acid vapours from gases derived from oxidized ammonia. June 13.

*Specifications published this Week.*

164762—Weizmann, C. and Spiers, H. M.—Fermentation of starchy material for the production of acetone and butyl alcohol.

164785—British Dyestuffs Corporation, Ltd., Green, A. J. and Porter, J. W.—Process of manufacture of phthalic acid and anhydride.

164803—Miersch, W.—Method of obtaining hydrofluoric acid from the sulphonating mixtures of organic sulpho acids and calcium fluoride.

145524—Akt-Ges. Fur Anilin Fabrikation.—Manufacture of cellulose esters of organic acids.

149688—Kuh, E.—Process for the production of neutral alkyl esters of sulphuric acid.

*Abstract Published this Week.*

*Gas Manufacture.*—Mr. H. Nielson and Mr. J. R. Garrow of 13, Firs Avenue, Muswell Hill and 30, Vineyard Hill Road, Wimbledon, both in London, have obtained a Patent No. 162459 for an improved plant for the distillation of carbonaceous material by contact with hot producer gas. A number of producers are used to consume the whole of the coke obtained, and only one producer delivers gas to the retort so as to avoid undue dilution of the coal gas, prior to the separation of tar oil. The coal is fed into a rotary retort, and the coke is discharged through an annular casing to a conveyor feeding the producers. The gas from a producer passes through the retort to a condenser and oil washer, and thence to an ammonia washer, to which the gas from auxiliary producers is led directly by a main.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

THE CHEMICAL NEWS.

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## PAPER-PULP SUPPLIES FROM INDIA.*

By WILLIAM RAITT, F.C S.

Cellulose Expert to the Government of India, attached to the Forest Research Institute, Dehra Dun, India.

(Concluded from p. 33).

IN proceeding now to review the economic side of the matter, let us disclaim at once any intention of basing estimates upon the present values of chemical wood-pulp. These are about £35 to £45 per ton c.i f. at British ports, according to quality, and undoubtedly represent temporary inflation. Any attempt to arrive at what may be the normal price of wood-pulp in this country when inflation has been worked off can only be a more or less intelligent appreciation of events, but considering that costs of production for labour, fuel, chemicals, machinery, freights, and wood are three to four times what they were in 1913, and that these advances are probably permanent, with wood still tending to rise, we shall not perhaps be far wrong in putting it at £28 per ton. If this is considered too high, the sequel will show that it is a figure permitting of considerable variation downwards. On similar grounds we would put the future normal price of mechanical wood-pulp—which is not cellulose at all, but only ground raw wood—at £16 per dry ton, Under the transport conditions I will describe later, bamboo can be delivered at manufacturing sites in Burma at a cost of 12s. 6d. to 15s. per dry ton, equivalent to from £1 11s. 3d. to £1 17s. 6d. per ton of unbleached pulp Compare this with the like cost for wood-pulp, which is from £10 to £12.

Manufacturing charges, inclusive of liberal allowances for depreciation of plant and contingencies, will be under £10 per ton of pulp, so that the total cost on board steamer in Burma ports will probably not exceed £12 per ton—about the cost of raw material alone in the case of wood-pulp. In freights, of course, wood-pulp, being nearer has the advantage, though not proportionally to distance, since port and terminal charges, no inconsiderable proportion of the whole, are the same for any distance. At present, from Burma ports, they are about £6, but this is abnormal, and I am advised on good authority that the eventual normal figure will not exceed £4. The prospects, therefore, are that bamboo unbleached pulp can be delivered in this country at a cost not eceeding £16 to £18. Freights, again, are not entirely a matter of export in this country. There is a growing demand for India, China, Japan, and Australia, and to these countries freights would be in favour of bamboo-pulp and against wood-pulp. The economic position thus disclosed has an interesting relation to mechanical wood-pulp, for which we have assumed a future normal value of £16 per ton. I do not think it has ever been seriously suggested before that a chemically-prepared pulp could be brought within competition distance in cost with a mechanical one, but the figures given above do now suggest such a possibility, and it is not wholly a question of price. Mechanical pulp will not produce a useful paper by itself, and it adds nothing to the quality of a sheet. It is merely a convenient filler, make-weight, and reducer of cost, and must be held together by a considerable admixture of true cellulose. No paper-maker uses it because he loves it, but solely because he *must* to get his cost low enough, and he will willingly substitute for it a true cellulose if it does not cost him very much more, especially since he is well aware that such a substitution enables him more effectively to use fillers, which are cheaper even than mechanical pulp, such as that good old stand-by, China clay.

Few industries are more sensitve to transport conditions. Including the product, six tons has to be transported in and out of a factory for every ton of product where coal is available If wood fuel is used, the total will be 8½ tons. It does not necessarily follow that each of the primary materials required—which are bamboo, fuel, limestone, and imported soda—must be available under ideal transport conditions. It may be the case that some extraordinary advantage in one of them enables the manufacturer to raise his cost limit for another, but it is evident that next to the raw material, transport is the ruling factor. Its importance may be illustrated by my own recent experience. During the past eight years I have been asked to revise some sixteen propositions for establishment of factories. Of these, only three failed on account of defects in the raw material supply, nine had to be rejected on transport conditions, and only four satisfied all requirements. Judging from enquiries I receive, this phase of the question receives little attention, and a sufficient supply of raw material appears to be popularly regarded as a satisfactory foundation for the industry.

In a previous paragraph I made a statement to the effect that India and Burma could produce ten million tons per annum under *possible* manufacturing conditions—possible, that is, with a normal value of £28 per ton in England—but the areas included in such a survey are naturally capable of being divided into best and second-best, and the best are probably not more than a fifth of the whole. They are to be found chiefly in the coastal belt of Burma and North-Eastern Bengal and Assam, with a smaller area in South-West India. I have myself explored a considerable area of the coastal region of Burma, where the transport conditions are nearly ideal—numerous rivers, many of them tidal to 100 miles from the sea, and with good rafting water above that intersected with creeks and connecting channels, and down which bamboo, felled upon their banks, can be floated to the manufacturing sites on deep water, or within easy reach of ports and anchorages by the aid of lighters. If wood fuel is not available—and it frequently is—coal from Calcutta or oil from Rangoon can be had, and limestone, also by water, exists at several places on the mainland or islands close to the coast. The only foreign import required carrying a high freight cost is the small amount represented by 15 to 20 per cent of the total soda consumption.

There is one peculiar feature of bamboo as to

*From *Journal of The Royal Society of Arts*, June 24, 1921. (By permission).

which a warning should be issued, viz., the extraordinary phenomenon it exhibits of cyclical gregarious seeding and death. A few species do follow the usual rule of grasses in annual seeding, and a few others seed sporadically, but most of the important ones flower in cycles of long period and gregariously, and each species has its own length of cycle. It goes on reproducing itself by shoots thrown up from the root year after year for 20, 40, or 60 years, until, feeling old age approaching, it throws all its remaining energies into producing an enormous crop of seed, and then dies. The new generation, although ultimately destined to produce culms which may be 120ft. in length, and 6in. in diameter at the butt, throws up a first crop of diminutive stems, perhaps 18in. high and less than a ¼in. thick. Next year brings a crop somewhat larger, and so on, increasing year by year in strict proportion to the growing power of the plant to produce starch and store it in its roots, until, after from four to ten years—the period varying with species, soil, and climate—it is again throwing up its full-sized culms. Note also, as a striking example of Nature's silent dynamic, that these stems which, as I have said, may be 120ft. by 6in., are produced of full height and diameter in four months. It is one of the few plants which you can literally see grow. Its branch and leaf system are developed in its second season, and it is then fully matured.

It will be clear from this that a factory planted in a district without some enquiry having been made as to the seeding cycle, might find itself suddenly bereft of supplies for a prolonged period. There are two methods of insuring against this; first, the next seeding period may be known to be at such a date that supplies can be depended upon for a period long enough to secure an ample return on capital invested in the undertaking, and, second, the presence in the area of an alternative species which, as is invariably the case, does not flower at the same period. It is satisfactory to be able to add that most of the important species have seeded within recent years, or are now in process of doing so, as if Nature had anticipated the demands we are about to make.

The crisis now threatening the paper industry, and, it may be added, the large and increasing family of industries based on cellulose, of which artificial silk and celluloid are types, is no unprecedented experience. It is historic and oft repeated. Beginning with the failure of rag to provide for a continually increasing demand, the trade during the last 100 years has passed in succession through the phases represented by the utilisation of textile wastes, straw, esparto, and wood, each in turn hailed as salvation, and each in turn failing to cope with the requirements or finding a better market. It remains a fundamental axiom of the industry that it is a "picker-up of unconsidered trifles." As the interests of other manufactures in a material increase so in proportion that of the paper-maker decreases. They can all pay more for it than he can. I have been trying for 25 years in various parts of the world to find a solution for this recurring trouble. As the final considered result of that experience, I venture to express the belief that no permanent solution of it can be found, except in the vast stores of annual—and I lay much stress on the annual—products of the forests and waste places of tropical and sub-tropical regions. Enormous in their volume, frequently co-existing with splendid transport and manufacturing facilities, continuous and rapid in their natural reproduction and easily converted by modern methods, they provide a field of enterprise of which we may well hesitate to prophesy the expansion and wholly fail to see the end. And remembering recent experience when we found ourselves almost wholly dependent upon foreign supplies, may we be pardoned for uttering a little pæan of congratulation that such areas are within the Empire?

DISCUSSION.

Mr. SINDALL then contributed the following observations: Mr. Raitt, in his address, shows that with regard to the preparatory treatment of bamboo for ultimate conversion into paper, two rival schools are in existence, which he describes as the "crushers" and the "chippers." The argument on behalf of the crushing school has been exhaustively presented, and it would, therefore, be interesting to know the line of argument adopted by the "chippers," so-called.

In this case, the stems of bamboo are passed through a special slab-wood chipping machine, which cuts the bamboo into small chips similar to those obtained by the treatment of slabwood. It is stated that such a process gives a much greater capacity in the digester, with a closer and better packing of the material. The digester is more easily and quickly filled, and owing to the closer packing of the material, less liquor is required. This, in its turn, means the use of a stronger liquor, and ultimately a much smaller quantity would need to be evaporated for the recovery of the soda. Messrs. Boving & Co., who have developed this system, state that they are able to fill a digester of a capacity of six tons by blowing in the chips in about half-an-hour. Experiments were made by them in Sweden on a large scale, some 20 tons of bamboo having been utilised for the purpose, and it has been proved that the product obtained is perfectly satisfactory.

This firm have given considerable attention to the question of economy in the production of esparto and bamboo pulp, and are at the present moment engaged in the erection of a large esparto plant in Scotland, based in the most modern practice of pulp treatment and the methods being introduced are certainly worthy of close attention on the part of paper-makers. The system as devised introduces many ingenious methods for economy in fuel and labour. The material is cut into small pieces, cleaned and dusted, and then blown into the digesters. The requisite amount of caustic soda is run into the digester, and the cooking proceeds by a new system of circulation. In present practice the material is cooked by blowing live steam into the mixture, with the result that the consequent condensation of the steam increases the volume of the liquor to be evaporated for the recovery of soda. In the new system the liquor is passed through the grass in the digester through an outside circulating system heated by high-pressure steam in such a manner that the steam condensed is drawn off separately and utilised for heating washing water or cooking liquor. The volume of liquor in the digester in this case is not increased and a definite saving is thus effected.

It is proposed to utilise this condensed steam for heating up the cooking liquor so that the pulp is at once supplied with hot liquor and this again means economy in steam.

When the pulp is sufficiently cooked, the pressure in the boilers is utilised to discharge or blow out the boiled grass direct to the washing tanks or diffusers. This method is substituted for the present system of allowing the steam to blow out into the air or into water. The practical result is that the black liquor containing all the non-fibrous organic compounds present in the original esparto has a density of something approximating 14° to 16° Twaddle as opposed to 6° or 8° Twaddle.

The clean pulp is flushed out of the diffusers by water, and passed over screens and sand traps similar to those employed for the production of wood pulp.

The whole process is continuous, requiring very little attention, and appears to be a great advance on the present system.

The same plant can be used and has been carefully designed for the treatment of bamboo. It appears that the knots in bamboo offer no difficulty, and certainly results obtained on such a large scale as that involved in the treatment of 20 tons should afford sufficient evidence as to the value of the method designed by them.

The most important development, however, in connection with esparto, bamboo, and similar materials such as Indian grasses, is the treatment of the black liquor obtained during the process of digestion. When these materials are treated with caustic soda, some 45 per cent to 50 per cent of the original matter is dissolved and the liquor is then highly loaded with organic matter.

In the earlier days of paper making this liquor was discharged into open streams and rivers of the neighbourhood, but owing to the action taken by local authorities it became necessary to devise some method of dealing with this black liquor, the discharge into streams and rivers being forbidden. A method was found in a process by means of which the liquor was evaporated to a thick consistency, in which condition the mass would catch fire and could be burnt, the organic matter in solution acting as fuel for a more or less complete incineration. The organic soda compounds were thus converted into crude carbonate of soda, in which form, after boiling with a definite proportion of lime, it was re-converted into caustic soda. The methods of evaporation, economy of washing water and scientific control of the several stages of treatment were gradually improved, and the recovery process, at first regarded as the outcome of a mere whim on the part of obnoxious local authorities, soon revealed itself as an important factor in reducing costs of production.

Of recent years, considerable attention has been given to a more scientific method of recovery in the hopes of obtaining more valuable bye-products than combustible matter. Rinman's process for the conversion of the soluble organic constituents into definite bye-products of commercial utility, already well established for wood pulps in Sweden, has now been applied in these recent experiments with bamboo, and an estimate of bye-products available from a standard bamboo pulp mill having a capacity of 10,000 tons air-dry pulp per year (using 22,000 raw material) is as follows:

| Bye-products. | Estimated kilos. | Price per kilo. | Total price. |
|---|---|---|---|
| 1. Methyl alcohol ... | 388,000 | 3s. | 46,200 |
| 2. Acetone used as petrol &c. ... ... | 330,000 | | |
| 3. Ethyl-methylketone (petrol) ... ... | 22,000 | 1s. | 38,500 |
| 4. Light oils (petrol) | 220,000 | | |
| 5 Heavy oils (Diesel oil) ... ... ... | 572,000 | 5d. | 11,917 |
| | 1,650,000 | | £96,617 |

or 1625 tons.

Rinman's process is carried out on the following lines. The black liquor already suitably concentrated to the required density is mixed with a small proportion of caustic soda liquor and a carefully calculated quantity of quick lime. This mixture when showing a density of about 40° Beaume is kept at a high temperature in proper storage tanks. The mixture is fed as required into a number of iron trays to the depth of about 2 cm. These trays fit into square shaped wagons, four of which are at one time pushed into the distillation furnace, which is perfectly airtight when closed up ready for the operation of distilling. The temperature of the oven is gradually increased to 200° C., the heat for this process being obtained by burning gases which are given off during the distillation process, any extra heat being obtained from a gas generator using coke. At 200° C. the excess moisture is driven off.

The temperature is raised to 300° C., and at this stage the bye-products given off are mainly crude methyl alcohol and hydrogen gas. These products are drawn off in a suitable manner.

At an increased temperature of 400° C., the bye-products obtained are acetone and light oils.

The whole operation of distilling occupies about 18 hours. The furnace is then cooled and the wagons drawn out of the apparatus, the contents of each trunk being tipped into water and causticised with lime. The lime mud, which is necessarily contaminated with the carbon left from the distillation process, is dried in a rotary furnace and ultimately burnt at a high temperature in another rotary furnace heated from the gas generator already described. By this means the lime mud is reconverted into quick lime which can be utilised over again in the process of causticising the crude carbonate of soda obtained from the distillation furnace.

If the Rinman process proves commercially practicable on a large scale as applied to esparto and bamboo, then the prospects for cheap bamboo pulp seem bright. The quantity of bye-products obtained as shown in the above table amount to nearly 10 per cent calculated on the original raw bamboo. At present the story reads like a fairy tale, but the fact remains that mills are being erected in Great Britain having all these new applications in view for the treatment of esparto and grasses and its application to bamboo is stated to be merely a matter of adaptation.

Mr. E. F. HEYERDAHL, of Christiania, said that last year he investigated the sulphate process and made trials with different materials. He had had a long experience in the treatment of coniferous woods, and he had also been to South Africa,

where a Norwegian company had a concession for the utilisation of papyrus. He carried out experiments with that papyrus, treating it by the sulphate process; and then made experiments with wattle wood and crushed wattle bark by the sulphate process. Recently he had made experiments with bamboo. The author proposed to carry out his digesting process in steps, first taking away the starchy matter and pectoses by boiling water and very diluted caustic soda. The author claimed that the action of the sodium hydroxide on the lignins did not take place before 130° C. That was right, and then most of the sodium hydroxide was already used up in dissolving the starch and the pectoses, but by the sulphate process there were two actual solvents on the lignine compounds, *i.e.*, sodium hydroxide and sodium sulphide. Sodium sulphide was a very strong resolvent for lignin, especially at high temperatures, and he believed that sulphide acted more strongly on lignin than sodium hydroxide, over 130° and 140° C. In treating bamboo, the sodium hydroxide would first dissolve the starch and the pectoses. That process would be completed at about 130° C., and then the sulphide would begin to act and would completely dissolve all the lignins in the bamboo. Another point about the sulphide was that it did not act upon the cellulose fibres, and, therefore, higher yields were always obtained when the sulphate process was used, about 5 per cent more yield on the material being obtained by using the sulphate process than by using the other process. When treating coniferous woods with sodium hydroxide, a brownish-coloured pulp was always obtained, owing to the fact that during the boiling the iron in the wood and the iron in the apparatus were dissolved by the sodium hydroxide and precipitated into the fibres. When the sulphate process was used, sodium sulphide dissolved all those iron precipitates, and a light greyish pulp was obtained instead of the brown pulp. In all his experiments he had only used bamboo chips, as he considered the crushing of the complete culms was not economical from a practical point of view; it required more power and he believed it was not good for the fibre. With regard to the yields, with the soda process, by a proportion of 19 to 20 per cent he had obtained 42 per cent of unbleached pulp, requiring from 16 to 18 per cent of bleaching powder on the pulp, and an average bleached yield of 37 to 39. With the sulphate process he obtained yields of from 43 to 45 per cent, with a consumption of bleaching powder of 12 to 14 per cent, the proportion of actual alkali ($NaOH$ $Na_2S$) being 18 to 20 per cent. When bamboo was cooked and made into a well-boiled pulp it was very easy to treat. The washing process was very easily carried out, as the water penetrated through the pulp very readily, and the washing time was reduced to about one-quarter of the time required on coniferous woods. Chipping the bamboo without considering the nodes was not good; there were too many nodes in the material and there would be a loss during boiling of about 5 to 6 per cent. The culms could be pressed in pressing rollers and then the pressed culms allowed to pass crushing rollers, which opened up the nodes and did not crush the internodes. The flat pressed culms with the crushed nodes could be chipped into chips of ¾in. to ⅞in. in length. By that process a loss of only about ½ to 1 per cent of the material would be obtained, and at the same time the actual capacity of the digester could be utilised to deal with about double the amount of material that could be treated if crushed bamboo were employed.

Mr. Heyerdahl exhibited to the meeting some samples of bamboo pulps.

Mr. Hamel Smith remarked that, having always been very keen on the utilisation of bamboo for paper making, he would like the author to say what sort of gospel it would be safe to preach to the tropics in the time to come. It was very easy tobe too sanguine on such points as had been outlined that afternoon, but after hearing a paper such as that which had been read, one realised the many technical difficulties which arose. Any one who had been used to sugar plantations could not help feeling that bamboos should be able to be cultivated on the same lines. One grew the cane within a certain area of the factory, taking good care to have the factory rather low down, if possible, because then the loads could be run down hill and the empty trucks up hill with greater facility. Also in regard to the question of transport, one should centralise the roadways or waterways so as to remove the finished product with greater facility. The experience on one estate, it seemed to him, might help on the other. Whether the production of paper from bamboo would ever become a private enterprise seemed a little doubtful. It was one of the queries he had often been asked, and he had never been able to give any satisfactory reply. Probably those who had been in the tropics would know that bamboo had been rather in bad odour on account of mosquitoes. The last estate he was on used to have the most beautiful bamboos surrounding it, but he believed that the medical authorities ordered them to be destroyed as they collected water after the rains, thus making a breeding place for mosquitoes. Would that sort of trouble rise in connection with large areas of cultivated bamboo for a factory? The sanitary authorities might raise the difficulty that the bamboos were inclined to encourage the presence of mosquitoes to a dangerous degree, and thus lessen the chances of final success.

Mr. Arthur Baker (Chairman of the Technical Section of the Paper Makers' Association) said the paper was the outcome of long and painstaking research in bamboo by Mr. Raitt, and showed what a great industry the paper trade was. In Canada and the United States the consumption of paper for newspapers alone was two million tons a year. Taking the question of bamboo and grasses, and considering it from the point of view of an industry which might be started in India, one had to look at the position of that country as a market. India was not a very big market for paper. He supposed that in pre-war days it used probably about 80,000 tons of paper a year, of which the Indian paper mills, some nine in number, produced about 32,000 tons. India had imported about 10 or 12 thousand tons of pulp, more than one-quarter of which had come from Germany and Austria. So that industry could not be started on any considerable scale. He agreed with the author as to treatment; he thought the sulphate process was undoubtedly the best, and that crushing was the correct method of dealing

with the raw material. If bamboo was to be a raw material for the paper-maker, it would require to be made on the spot, as the sulphate process created rather objectionable odours which would not be tolerated in all communities. He thought bamboo would obtain a foothold in India for printings, and it might be exported to Australia, China, and even South Africa. The question of the use of all new fibre materials resolved itself into a £ s. d. proposition. Unless bamboo could compete strictly with other raw materials, on a £ s. d. basis, it would never become an industry either in India or anywhere else.

Mr. ROLAND GREEN said that during the war they had used bamboo by crushing under a power hammer and boiling it in esparto boilers, where they had not more than 50lb. pressure. The conditions were not at all good; it wanted higher pressure and longer boiling. But they had found it quite satisfactory, and had had no trouble at all after the crushing had been arranged.

Mr. L. P. ANDREWS said it seemed to him that bamboo was a most extraordinarily easy material to handle, and he could not help thinking that it was going to be a great factor in the future.

Sir JOHN G. CUMMING, K.C.I.E., C.S.I., in proposing a vote of thanks to Mr. Raitt for his paper, and to Mr. Sindall for his kindness in reading it, said it had been known to him for many years that Mr. Raitt had been making researches in India regarding the possibilities of paper-making. Mr. Raitt, the Forest Research Institute, and the Department of the Government of India which controlled that Institute (of which the Chairman that afternoon had been one of the most distinguished members), deserved great credit for what had been done in that direction. His own interest in the matter was two-fold. He had been over a great part of the area both in Bengal and Burma, to which allusion had been made, wherein bamboo forests of the nature required were to be found. Secondly, he was intensely interested in any form which industrial expansion in India might take.

Mr. G. M. RYAN, F.L.S., late Indian Forest Service, in seconding the motion, enquired whether other plants and grasses had been examined for the purpose of finding out whether they were suitable for paper-making? For instance, there was one plant, a common weed really, which he thought might be utilised for pulp and which could be obtained in very large quantities in India, namely, *Calotropis*. The fibre was already of use, but with the bark combined, he thought it might be made applicable for paper. He, therefore, would like to ask Mr. Sindall whether it would not be possible to use it for the purpose of paper, as it contained a large amount of cellulose? With regard to bamboo unfortunately nearly all the areas where bamboos grew were really on poor soil and unfit for agriculture, so that he did not think private enterprise could develop the industry. Government would have to organise the areas referred to especially for paper. There was a very large demand in India for bamboo for huts, &c. Therefore, in considering the amount of bamboo which would be available for paper, a large quantity would have to be deducted for local needs. It would not do to infringe on the existing economic uses of bamboo. May years ago in a district in the Bombay Presidency there used to be an area of about 500 square miles extensively covered with bamboo forests, which had now disappeared, owing to the large demand for bamboo for dwellings of the people. He thought these forests be resuscitated and that no effort should be spared by the Government to do this. Another important thing was fuel supply. Wood was in large demand in India, and the problem was how to get it for burning in the paper factories. Recently there had been discovered a means by which waste vegetation could be converted into solid fuel by the Wells process which had been established in Egypt. Half-a-million acres of ground had been taken up there for cultivation, and the scheme was first of all to grow waste vegetation to feed the machines which would convert it into solid fuel. For the purposes of transport, and other means, those machines would be of great use in manufacturing fuel from waste products around the paper-pulp factories; and he wished to point out what a great advantage the new process would be for India as regards obtaining fuel in this way.

Mr. SINDALL, in replying to the vote of thanks, said that one or two interesting points had been raised on the general issue. He thought all were agreed that it was not a question of technical difficulty at all. The matters arising out of the actual treatment of the bamboo and the technical problems involved had been very largely settled. Nor were there any rival methods in use. As Mr. Baker had said, the whole question was one of £ s. d.—whether it was commercially possible. No private enterprise could possibly succeed unless there was a prospect of profit, and that was all the paper-maker or the pulp-agent was concerned with. With reference to the amount of bamboo available, the point raised by Mr. Ryan was an important one, because bamboo certainly had a distinct market value in the towns, and one would necessarily therefore be compelled to seek such regions in which bamboo was growing freely and where the cost involved was merely that of cutting down and collecting. It followed, therefore, that there would not be cultivation of bamboo as ordinarily understood, but a proper control of growth in areas allocated to or belonging to the mill. With respect to grasses, they were being used in large quantities by several mills. The difficulty with some of the grasses in India was that the yield was very low, and therefore it was not a commercial proposition. The question of the suitability of bamboo in paper-making had been settled long ago. He supposed the reason why private enterprise had been rather backward in the matter was because it cost £100,000 to £150,000 to put down even a small mill in an enterprise regarded as somewhat speculative.

## UNIVERSITIES, RESEARCH, AND BRAIN WASTE.*

By J. C. FIELDS, Ph.D., F.R.S.

(Continued from p. 36).

IN the boy of promise, too, France sees the future man and treats him as a potential asset. He does not need to stop short in his education because his parents are poor. There are bourses awaiting him from the Commune, the Department, and the

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Government. Where his gifts justify it, he will be provided with the best education which the country can offer. In the advanced classes of certain Lycées as many as 75 per cent of the pupils hold bourses. The Government maintains schools of university grade for genius. Entrance to these schools is by competitive examination, and the number to be admitted each year is limited. Such schools are the Ecole Normale Supérieure and the Ecole Polytéchnique. In the Ecole Normale literary and scientific studies are both provided for. On the literary side the nmber admitted annually is limited to 30; on the scientific side to 22. The number of candidates for admission in science is normally about 150, all young men of exceptional ability. Of these then about 85 per cent are rejected. It is to be noted also that of those accepted, many will have made the attempt more than once. Conditions are pretty much the same in regard to the literary candidates. The students at the Ecole Normale follow the lectures at the Sorbonne. They also have special courses of their own, which are sometimes supplementary to those of the Sorbonne. They live in residence, study under direction, have a library at their disposition, and work in their own laboratories. After three years in residence, the students are again sifted by examination. The most gifted are directed toward the career of the university professoriate. The others supply a brilliant nucleus for the teaching staffs of the Lycées. Those students whose way has been paid by the Government are under obligation to take service with it for ten years, and it in turn is under obligation to furnish them with employment. Half the students at the Ecole Normale are under these conditions.

The number admitted annually to the Ecole Polytéchnique is in the neighbourhood of 200. These would normally constitute about 20 per cent of those who write on the examination for entrance. The course at this great engineering school lasts for two years, after which the student is sent on to the Ecole des Mines, the Ecole Centrale, the Ecole d'Artillerie, or some other school for a practical course. Of this school Joffre, Foch, Pétain, Nivelle, and others of the more notable French generals in the war just past are graduates. It was with a certain satisfaction that one learned that a Frenchman had been appointed General-in-Chief of the Allied Armies; for it was practically certain that he would be a graduate of the Ecole Polytéchnique. This would be a sure guarantee of his intellectual calibre, for he would be select among the select. One could rest assured, too, that on top of his course at the Ecole Polytéchnique he would have received an advanced technical training proportioned to his natural ability.

There is a strong mathematical trend to the training given in the Ecole Polytéchnique and it is quite remarkable what a number of famous mathematicians have been turned out by this school. It is hardly necessary to add that graduates of the school whose way has been paid by the Government are under obligation to take service with the Government. The Government, too, finds good use for their services, not alone as officers, but also in important civil capacities.

The candidate who fails to obtain entrance to the Ecole Normale or the Ecole Polytéchnique may have better success with the Ecole des Mines, or the Ecole Centrale, schools also with limited admission. In any case there will be nothing to prevent him hearing lectures at the Sorbonne, for attendance on the courses given there is not limited as at the other schools I have mentioned.

In England it will shortly be as in France that the boy of exceptional ability will be able to pursue his studies as far as he will, however indigent the circumstances of his parents may be. At present there is nothing to prevent him completing his course in the secondary school, for plenty of scholarships to that end are offered by the county councils. There are also more than enough scholarships in classics for entrance to the universities. In science and moderns, however, such scholarships are lacking The funds to redress the balance here have been promised, so I am told, and it will not be long until arrangements have been made which will provide for carrying the boy of outstanding ability right through the secondary school and the university, or higher technical institution of university grade, and training him for research if his tastes incline that way.

The experience of the Naval Dockyard Schools in England furnishes an interesting commentary on the amount of brain waste there must be in classes of the community where better educational opportunities are not available. The schools here referred to are conducted for the benefit of shipwright apprentices who work in the Dockyards. The apprentices who distinguish themselves in their studies are transferred to the Engineering College at Keyham for a year, and if their showing justifies it, they are then sent on to the Royal Naval College at Greenwich for the three years' course at that Institution.

The majority of the present Constructive Staff at the Admiralty Dockyards were formerly students at the Dockyard Schools. These same schools have furnished a succession of distinguished Directors of Naval Construction at the Admiralty. Among these one might mention Sir William White, the designer of the pre-Dreadnoughts, and Sir Philip Watts, designer of the first Dreadnought; others are Sir E. Reed, and Sir N. Barnaby. Sir J. Marshall, who started as an apprentice in a Dockyard school, became, later on, Director of the Dockyard. Sir J. Biles, Professor of Naval Architecture at Glasgow, had the same start, and this was the case also with Mr. S. J. P. Thearle, formerly Chief Surveyor of Lloyd's. Others could be named who have occupied or who are at present occupying commanding positions with some of the largest private shipbuilding concerns in Great Britain.

What a pity it would have been had such precious material been lost to great Britain. What a pity it is that so much material of like character has been lost and is being lost to Great Britain and the Empire. What a pity it is, too, that in Canada no adequate effort has been made to salvage equally good material.

The indications are that Great Britain will, in the near future, realise more largely on her latent intellectual resources than she has done in the past. To compete with Germany in technically trained men, however, she will have to increase the flow of students from the secondary schools to the universities and higher technical institu-

tions by every means at her command. Mr. Fisher's Education Bill will help greatly to that end when it comes completely into force seven years hence. Under its provisions a pupil who has reached the age of 14 years of age will have the alternative of continuing his studies on full time for two years longer or of studying part time until he reaches 18. This will bring him to within sight of entrance to the university. The indications as to who should take a university course ought to stand out fairly definitely by this time, and the scholarships referred to above, will, no doubt, make their appeal to the ambitionus student.

In a recent number of *Nature* (August 15, 1918), Prof. R. A. Gregory has given some figures with regard to the relative attendance at universities in England, Scotland, Wales, and Ireland, the United States, and Germany, from which a little analysis will draw rather interesting conclusions. The number of university students per 10,000 population is approximately 14 in Germany, 10 in the United States, 5 in England, 17 in Scotland, 7 in Ireland, 6 in Wales. In giving the figure for the United States, Prof. Gregory has based it on the 72 universities on the accepted list of the Carnegie Foundation. In Canada, as a whole, the figure would be about 15, and in Ontario it would bulk somewhere in the neighbourhood of 25. Here no account has been taken of the difference in standards for entrance to the universities in different countries, or of the difference of age at which the student is prepared to enter. In Germany the average age at which the student leaves the gymnasium is between 20 and 21. In Great Britain the usual age of entrance to a university is between 17 and 18, except in the case of Oxford and Cambridge, where it is between 19 and 20. With us, the normal age of matriculation is 18, and it is about the same in the United States. Taking these facts into account, it will be seen that most of that which passes as university work in Great Britain, Canada, and the United States would be of gymnasial standard in Germany. If we would compare the number of students in the several countries, on the basis of the university standard in Germany, we would probably not be doing injustice to any of the other countries concerned by giving for every 10,000 of population the figures 14 in Germany, 3 in the United States, 3 in England, 6 in Scotland, 3 in Ireland, 2 in Wales, 5 in Canada, 8 in Ontario.

While in Paris last summer, I found that the total attendance for the year 1913-14 at universities and other educational institutions of university grade in France was in the neighbourhood of 26,000. This is at the rate of a little more than 6 per 10,000 population. It would hardly be necessary to cut this figure down as much as we did with the corresponding figures for other allied countries. In comparing the university status of France with that of Germany, too, it would only be fair to take account of the selective policy adopted by the former country with regard to the intellectually gifted.

One must not be too hasty in finding implications in the figures we have mentioned or in drawing conclusions from them. They do not imply that the intellectual status of Germany compared with that of England is as 14 to 3, nor do they give the relative positions of the two countries in regard to scientific achievement. The scientific status of a country is determined principally by the quality of the output of its foremost research workers. The status of England in science compared with that of Germany is in the aggregate, no doubt, higher than that given by the ratio 3 to 14. This would seem to indicate that among the scientists trained in England is to found a larger proportion of high grade ones than is the case with those who are trained in Germany. This may or may not imply a smaller proportionate waste of scientific material among the men of highest intellectual capacity in England than among those who are of a somewhat lower grade. It might imply that the average intellectual level of the classes in England from which the ranks of science are recruited is higher than that of the classes in Germany from which science draws her recruits. My own impression is that the average Englishman has been endowed by nature with more intelligence than the average German. There can be no doubt that the amount of brain power which is undeveloped and which goes to waste in England is something enormous. The one thing that the figures just given do tell us is that in Germany there are more young men in proportion to population who prolong the period of their studies and receive an advanced training than there are in other countries. Of these young men science secures its full share. As a consequence, a larger number of highly trained men are available for the purposes of science and industry in Germany than elsewhere. It would appear that men of such training have been spared by Germany during the war as they have not been spared by the Allies.

Two months ago, while in London, I had a conversation with Dr. E. C. Worden, chemical expert of the Bureau of Aircraft Production, Washington, D.C., who had been commissioned to report on the chemical factories in the occupied portion of Germany. He had furnished detailed reports on 62 chemical factories. The largest of these was the factory of the Bayer Company, at Leverkusen, 12 miles from Cologne. At this factory over 3,000 tons of pharmaceuticals, dyestuffs, and other chemicals were awaiting export. The plant is equipped with 3,500 telephones. At the time of Dr. Worden's visit, over 500 research chemists were at work, and to these several hundred more would be added as soon as the raw materials were available. According to Dr. Worden, Germany kept her technical forces unimpaired by the war. She placed her technical men in positions where they did not run too much risk.

An economic blockade has been divested of some of its terrors for the Germans, for the Haber process has been so improved that they can obtain an ample supply of nitrates from the air. Their agricultural needs in this connection, Dr. Worden states, will be satisfied for all time. At the Badische Anilin und Soda Fabrik, located near Ludwigshafen, above Coblenz, on the Rhine, they are in a position to extract the nitrogen from 2¼ cubic miles of air daily. This company has a new research laboratory which, with its equipment, cost $750,000. In many cases where the Germans used a chemical plant for making explosives, they erected in the neighbourhood a substantial factory on a scale at least equal to

that of the plant which was being utilised for war purposes, and the factories so erected were all held in readiness to begin operations as soon as the war was over. The expectation was, of course, that these new plants would be paid for by the Allies, and no expense, therefore, was spared in their preparation. It is hardly necessary then to remark that Germany, so far as the chemical industry is concerned, is in splendid condition to resume competition with the other nations of the world.

It evidently behoves the Allies to increase not only their university attendance, but more particularly also their output of research workers. This would be advisable under any circumstances. It becomes doubly urgent in the face of a German competition backed by an ample supply of scientifically trained workers. Nowhere is it more necessary to take stock of one's scientific position than it is in Canada.

The figures already given for university attendance do not appear to place Canada in an unfavourable light as compared with countries other than Germany. Gauged by the second set of figures, however, Canada as a whole, and even Ontario, show to disadvantage in comparison with Germany. The actual diadvantage, too, is greater than that implied in the ratio of 8 to 14. For the 8 Ontario students would, on the average, be less mature than the 14 German students, and would include among them a smaller proportion who are engaged on more advanced work, and preparing to do research. If we limit ourselves to the upper ranges of University work, that is to say, to the preparation of research workers, Canada hardly compares with the United States, and Ontario itself is quite outclassed by certain States of the Union. It may be remarked, however, that we in Ontario are getting under way.

I have referred to the assistance in the form of scholarships and bourses extended to the poor boys in England and France We have nothing that corresponds to this in America. Our idea of a scholarship is a comparatively small prize not at all proportionate to the keep of a boy for a year, let alone several years in succession. Our nearest approach to the English conception of a scholarship is what we call a fellowship. This, however, is only available to a graduate student. The attached stipend is usually a meagre one, and the fellowship may or may not be renewable for a second or third year. It is often utilised, too, as a pretext for securing a certain amount of cheap teaching.

(To be continued)

## THE REVISION OF THE ATOMIC WEIGHT OF LANTHANUM.

### Preliminary Paper—The Analysis of Lanthanum Chloride.

By GREGORY PAUL BAXTER, MUNEO TANI, and HAROLD CANNING CHAPIN.

In line with the recent determinations of the atomic weights of neodymium (Baxter and Chapin, *Journ. Am. Chem. Soc.*, 1911, xxxiii., 16; Baxter, Whitcomb, Stewart and Chapin, *ibid.*, 1916, xxxviii., 302), and praseodymium (Baxter and Stewart, *ibid.*, 1915, xxxvii., 516), the atomic weight of the closely related element, lanthanum, has been subjected to investigation by a method essentially identical with that used for the other two elements. This investigation was begun independently by Chapin, who purified by fractional crystallisation a considerable quantity of lanthanum material and began the analysis of the chloride. A second sample of impure lanthanum salt was fractionated in a similar way by Tani. Although it has not been possible to complete the analysis of a sufficient number of fractions of material to fix the atomic weight of lanthanum beyond question, yet since the work has been interrupted for an indefinite period, the preliminary results are presented in a brief fashion.

*The Purification of Lanthanum Salt.*

The purification of the lanthanum material was effected by fractional crystallisation of the double ammonium nitrate. The original material used by Chapin was very kindly furnished by Dr. H. C. Miner, of the Welsbach Light Company. The material fractionated by Tani consisted of the less soluble portions resulting from the fractionation of crude praseodymium ammonium nitrate (Baxter and Stewart, *loc. cit.*), which also had been furnished by Dr. Miner for the previous investigation on praseodymium.

According to Auer von Welsbach, in the crystallisation of the double ammonium nitrates, the bases separate in the order, lanthanum, cerium, praseodymium, neodymium, samarium, terbium, and ytterbium earths (A. von Welsbach, *Sitzungsb. Acad. Wiss. Wien*, 1903, cxii., 1043). Because the lanthanum separates at the head of a series of fractions the purification of lanthanum is simpler than that of any other rare earth. It is also economical of material, because rejection of fractions containing impurities is necessary at only one end of the series. The fractionation was carried out by dissolving the double nitrate in a very dilute solution of nitric acid and allowing the salt to crystallise. The crystals were then dissolved and recrystallised; the mother liquor was evaporated to crystallisation. The mother liquor of the less soluble fraction was now combined with the crystals of the more soluble and the process continued until the number of fractions was 12 or more. The mother liquor of the most soluble fraction was frequently rejected The crystals from the least soluble fraction, as soon as it became small, were, in the case of Chapin's fractionation, separated and preserved to be united later with similar fractions, but the mixture was never returned to the fractionation series. In Tani's fractionation, as soon as the least soluble fraction became very small, it was set aside, and later added to the extreme fraction of a later series of crystals, so that no material was removed from the less soluble end of the fractionation series.

In Chapin's fractionation, 96 series of crystallisation were made, involving over 2300 fractions. In Tani's fractionation, although the number of series of crystallisations was the same, the total number of fractions was only somewhat over 1100, owing to the more frequent rejection of the most soluble fraction. The final series contained 39 fractions in Chapin's, 12 in Tani's fractionation.

The crystallisation was continued in both cases until the most soluble fraction, when its absorption spectrum was examined, seemed to be free

from praseodymium. Furthermore, the most soluble fraction in the last series of Tani's material, No. 12, was tested for cerium by passing chlorine into a suspension of its hydroxide in dilute aqueous sodium hydroxide. The cerium dioxide remaining was found to represent about 1 per cent of the whole fraction. Fraction No. 8, in the last series of crystallisations, when examined in the same way, gave no indication whatever of cerium. Since the atomic weights of cerium and lanthanum are separated by only a single unit, even 1 per cent of cerium would affect the average atomic weight of the mixture by only one-hundredth of a unit, hence the first eight fractions must have been amply pure for the purpose. The absence of cerium, since it falls between lanthanum and praseodymium in the order of separation, insures the absence of praseodymium as well.

The arc spectra of the different fractions were examined by photographing the ultra-violet region, λ5000-2200, with a Féry quartz spectrograph. Pure graphite electrodes were used. In the spectrogram of Tani's Fraction No. 11, which must have contained less than 1 per cent of cerium, the lines of this element were plainly visible, but in the case of Fractions 1 and 5, even the presence of the stronger cerium lines was doubtful. This was also the case with Chapin's fractions 3 and 4.

*The Preparation of Lanthanum Chloride.*—Selected fractions of material were converted to chloride in a fashion identical with that used in the case of neodymium and praseodymium, as follows. Lanthanum oxalate was precipitated with an excess of oxalic acid and the precipitate was washed, dried, and ignited in an electrically-heated muffle to a mixture of oxide and carbonate. Then the oxide was dissolved in nitric acid and the process repeated twice. The ignited oxide was now dissolved in a quartz dish in hydrochloric acid which had been distilled through a quartz condenser. After the solution had been evaporated to small bulk, the salt was separated by saturating the solution at zero degrees with hydrogen chloride conducted to the solution through a quartz tube. Centrifugal drainage followed, and then the salt was recrystallised four times in the same way. In order to remove superficial water as far as possible, it was left in a vacuum dessicator over fused potassium hydroxide for some time, with occasional crushing in an agate mortar.

All of the reagents were carefully purified by processes that have been described in some detail in the papers on atomic weights of neodymium and praseodymium.

*The Drying of Lanthanum Chloride.*—In order to prepare the lanthanum chloride in as nearly as possible an anhydrous condition, the crystal water was first removed by a series of processes of efflorescence, and the salt was finally fused as rapidly as possible in a current of dry hydrogen chloride. As has been pointed out previously (*Journ. Am. Chem. Soc.*, 1915, xxxvii., 527), it is of vital importance that the moisture be removed as far as possible at a low temperature before the final fusion, otherwise basic lanthanum chloride forms in appreciable quantities. The transition temperature of the heptahydrate we found to be about 91°. Therefore, until the greater part of the crystal water had been expelled, the temperature was maintained below 85°. Then the temperature was raised to about 130°, where the last molecule of crystal water evaporates. As soon as this process apparently was complete, the temperature was raised to about 360°, and kept at this point for some time. Finally, the salt was fused as rapidly as possible by means of an electrically heated sleeve. The salt was probably heated to nearly 1000° in this operation, for Bourion (Bourion, *Ann. chim. phys.*, 1910, [8] xx., 547) found the melting point to be 890°. During the drying the salt was contained in a platinum boat placed in a transparent quartz tube connected with a glass-bottling apparatus, which is essential for the subsequent handling of hygroscopic salts. (Richards and Parker, *Proc. Am. Acad.*, 1896, xxxvii., 59).

After the fusion of the lanthanum chloride it was allowed to cool rapidly, and the hydrogen chloride was displaced by nitrogen, and this in turn by air. Then the boat was transferred from the quartz tube to the weighing bottle without exposure to moisture, and weighed.

In some instances the salt gave a perfectly clear solution in water; in others, owing apparently to difficulty and delay in attaining the rather high fusing point of the chloride, traces of insoluble material were visible. Although not analysed, there is little question that this was the basic chloride, for both neodymium and praseodymium chlorides, under similar circumstances, become slightly basic (*Jour. Am. Chem. Soc.*, 1915, xxxvii., 527; 1916, xxxviii., 305). The quantity of insoluble material apparently never exceeded a few tenths of a milligrm., and on allowing the solution to stand for a day or two, the basic salt dissolved completely in most cases.

*The Method of Analysis.*

The method of analysis was like that previously used with neodymium and praseodymium and other chlorides. The salt was dissolved in water and the solution was diluted to a volume of 1000 to 1500 cc. in a glass-stoppered precipitating flask. Pure metallic silver, equivalent to the chloride within a few tenths of a milligrm., was weighed out, dissolved in nitric acid and diluted to about the same volume. The silver solution was then added to the chloride solution in small portions, with frequent agitation. After standing at room temperature for some time, the clear solution was tested in a nephelometer for excess of chloride or silver. The estimated deficiency of either was added in the form of 0·01 *N* solution, and the solution was again thoroughly shaken, allowed to clarify and tested as before, and the process was repeated until exactly equivalent quantities of silver and chloride had been used. In computing the quantity of silver equivalent to the chloride, allowance was made for solution removed and not returned in the nephelometric tests. In all but one of the analyses several months intervened between the precipitation and the final adjustment of equilibrium, so that occluded material had abundant opportunity to be leached out.

After the end-point of the comparison had been established, an excess of 0·05 g. of silver nitrate was added for each litre of solution and the analyses were allowed to stand some time longer. Then the silver chloride was washed several times

## The Atomic Weight of Lanthanum.

Series I. $LaCl_3 : 3Ag$ Ag = 107·880. Cl = 35·457.

| No. of Analysis. | Analysis. | Fraction of $LaCl_3$ | Wt. of $LaCl_3$ vacuum. G. | Wt. of Ag in vacuum. G. | Wt. of Ag added or substracted. G. | Corrected Wt. of Ag in vacuum. G. | Ratio $\frac{LaCl_3}{3 Ag}$. | Atomic Wt. of lanthanum. |
|---|---|---|---|---|---|---|---|---|
| 1. | Chapin ... .. | C27 | 3·45559 | 4·55597 | +0·00353 | 4·55950 | 0·757888 | 138·910 |
| 2. | Tani ... ... | C3+4 | 5·75303 | 7·59221 | −0·00087 | 7·59134 | 0·757841 | 138·897 |
| 3. | Tani .. ... | C3+4 | 8·18782 | 10·80358 | +0·00003 | 10·80361 | 0·757878 | 138·909 |
| 4. | Tani .. ... | T1 | 6·80122 | 8·97404 | −0·00045 | 8·97359 | 0·757915 | 138·921 |
| 5. | Tani ... ... | T1 | 6·73670 | 8·88887 | −0·00058 | 8·88829 | 0·757930 | 138·925 |
| 6. | Tani ... ... | T5 | 5·43254 | 7·16816 | −0·00044 | 7·16772 | 0·757919 | 138·922 |
| | | | | | | Average, | 0·757895 | 138·914 |

Series II. $LaCl_3 : 3AgCl$.

| No. of Analysis. | Analyst. | Fraction of $LaCl_3$ | Wt. of $LaCl_3$ in vacuum. G. | Wt. of AgCl in vacuum. G. | Loss in wt. on fusion. G. | Dissolved AgCl. G. | Corrected Wt. AgCl in vacuum. G. | Ratio $\frac{LaCl_3}{3 AgCl}$. | Atomic wt. of lanthanum. |
|---|---|---|---|---|---|---|---|---|---|
| 7. | Chapin ... ... | C27 | 3·67748 | 6·44443 | 0·00014 | 0·00129 | 6·44558 | 0·570543 | 138·969 |
| 8. | Tani ... ... | C3+4 | 5·33464 | 9·35196 | 0·00042 | 0·00101a | 9·35255 | 0·570394 | 138·905 |
| 9. | Tani ... ... | C3+4 | 5·75303 | 10·08459 | 0 00029 | 0·00181 | 10·08611 | 0·570391 | 138·904 |
| 10. | Tani ... ... | C3+4 | 8·18782 | 14·35541 | 0·00041 | 0·00125 | 14·35625 | 0·570331 | 138·880 |
| 11. | Tani ... ... | T1 | 6·80122 | 11·92149 | 0·00017 | 0·00200 | 11·92332 | 0·570405 | 138·909 |
| 12. | Tani ... ... | T1 | 6·73670 | 11·80828 | 0·00021 | 0·00145 | 11·80952 | 0·570438 | 138·924 |
| 13. | Tani .. ... | T5 | 5·43254 | 9·52361 | 0·00022 | 0·00124 | 9·52463 | 0·570368 | 138·893 |
| | | | | | | | Average, | 0·570410 | 138·912 |

(a) The concentration of AgCl in the aqueous washing was assumed to be the average of that found in the other experiments, 0·00120 g. per litre.

with silver nitrate solution containing 0·05 g. per litre, and many times with cold water, before being collected on a weighed platinum-sponge Gooch crucible. The chloride was dried in an electrically-heated air-bath at 290° for at least 18 hours and weighed. Residual moisture was determined by the loss in weight when the main bulk of the precipitate was fused in a porcelain crucible. The weight of silver chloride dissolved in 1 litre of the filtrate and silver nitrate washings, was assumed to be 0·00005 g. per litre (calculated from the solubility product of silver chloride at 20° as found by Kohlrausch, $1 \times 10^{-10}$, *Z. physik. Chem.*, 1908, lxiv., 167). Chloride dissolved in the aqueous washings, together with that obtained from the precipitating flask by rinsing with ammonia, was estimated by nephelometric comparison with standards.

In most of the experiments the portions of the original solution removed for nephelometric comparisons were rejected, and a correction of 0·00015 g. was added for each 100 cc. of solution removed. In a few experiments the test portions were returned and a correction applied for the silver chloride thus introduced.

All objects were weighed by substitution for similar counterpoises, a No. 10 Troemner balance being used for the purpose. Weights were standardised to hundredths of a milligrm. by the Richards substitution method (Richards, *Journ. Am. Chem. Soc.*, 1900, xxii., 144). The following vacuum corrections were applied.

| | Specific gravity. | Vacuum correction per G. |
|---|---|---|
| Weights ... ... ... | 8·3 | ...... |
| $LaCl_3$ ... ... ... | 3·947a | +0·000159 |
| AgCl ... ... ... | 5·56 | +0·000071 |
| Ag ... ... ... ... | 10·49 | −0·000031 |

(a) Matignon, *Compt. Rend.*, 1905, cxl., 1339.

The foregoing table includes all the experiments made by Chapin and Tani. Two analyses made by W. A. Turner with another fraction are not included because the fused salt and its solution were not satisfactory in appearance.

The average atomic weight of lanthanum found by us, 138·91, is nearly one-tenth of a unit lower than the value selected by the International Committee on Atomic Weights, 139·0, but just as much higher than the value 138·8 calculated by Clarke (Smithsonian Misc. Coll., "Constants of Nature," Part V. "A Recalculation of the Atomic Weights," 1910, 493). Nearly all the earlier determinations depend upon the results of methods in which lanthanum oxide plays an important rôle. The recognised difficulty of preparing rare-earth oxides free from traces of the compounds from which they are made by ignition is probably a chief cause of the wide variation among earlier determinations.

It is to be noted that the presence of the usual companions of lanthanum, namely, cerium, praseodymium, and neodymium would raise the apparent atomic weight of lanthanum so that the value obtained in this investigation unquestionably represents a maximum.—*Journal of the American Chemical Society*, May, 1921.

## ABSTRACTS OF SOME RECENT FOREIGN PATENTS.

Norway.—Urea being a very good fertiliser, various methods have been proposed for its production. Commercial cyanamide has been the principal material employed, it having been proposed to treat it with an acid or different acid salts. The use of acids, however, is very expensive and inconvenient. One might suppose that when commercial cyanamide or neutral or basic salts is treated with water, the cyanamide, owing to the presence of water, is converted into di-

cyanamide or ammonia. According to a recent invention by M. Egil Lie and the North-Western Cyanamide Co., of Norway, the surprising discovery has been made that urea can be obtained by employing soluble salts of alkaline or alkalino terreous metals, without the use of acids. (517900).

Humid nitrate of urea being very acid, is not satisfactory when utilised as a fertiliser, owing to the action of this acidity on the soil, and the fact that the bags in which it is packed are liable to be destroyed in damp air. All this is remedied, it is claimed, by the "Narsk Hydro-Elektrisk Kvaelstofaktieselskab" by mixing the nitrate of urea with carbonate of lime. When this fertiliser is put into a humid soil and the components of the mixture begin to act, nitrate of lime is formed, an excellent fertiliser, especially in a soil poor in lime. Free urea is also an excellent fertiliser. Then carbonic acid gas is produced, which dissolves the other plant foods, without attacking the roots. (517478).

BELGIUM.—An invention for utilisation of sewage, night-soil, &c, by M. V. D. Steyaert, consists in incorporation of bisulphate of soda, $NaHSO_4$, with the crude materials. Thus the ammoniacal matter is transformed into a solid odourless product, which can be put into bags and kept without loss of nitrogen, and is sufficiently rich in fertilising elements. A specially constructed plant is employed from which the dry fertiliser makes its exit. (517548).

HOLLAND.—A Dutch inventor, Mr. A. Messerschmitt, discovered that it is possible to decompose certain rocks containing potash, especially leucite, so rapidly and profoundly, by heating them with solutions of salts of soda at a high temperature and under pressure, that the reaction is practically utilisable to obtain potassic fertilisers soluble in water and pure potash salts. If, for example, a finely pulverised leucite slime is heated with a solution of soda salts in autoclaves under pressure, provided with agitators, the potash in the rock is displaced by soda, and a mixture is obtained formed of an aqueous solution containing the separated potassium salt and residues soluble in water, which after removal of the soda can yet give potash. The slime when dried gives a fertiliser of great value. (578368).

## NOTES.

THE JOHN FRITZ MEDAL, the highest honour that can be conferred by the American engineering profession, has been presented to Sir Robert Hadfield. In presenting the medal, the American societies "express their high regard and appreciation for what the British engineers did in the war for the preservation of civilisation."

THE *Analyst* for July contains an important paper by John C. Thresh, M.D, D.Sc., F.I.C., on the "Action of Water upon Lead." A great many carefully conducted experiments are described, and as the matter is one that the late Sir William Crookes devoted much time to, on account of its great national importance, we draw attention to the following conclusions arrived at by the author: "The experiments recorded prove that water has no action whatever on lead; that it is the foreign matters dissolved in water which affect the metal, the oxygen combining with it to form a soluble oxide or hydroxide, which remains in solution (to the point of saturation) in the absence of other substances capable of combining with it. This solution is of a colloidal nature, and of such coarse degree of dispersion or so liable to adsorption that it will not pass through a Pasteur filter, and may not even pass a fine paper filter. In the presence of acids forming soluble lead salts, such salts are formed, and will pass through any filter. If the acid forms insoluble salts, these are thrown down, and may be deposited on the metal in such a way as to prevent any further action. Any soluble salts present in the water may likewise act upon the lead hydroxide. Water is merely an inert medium, by means of which these foreign substances are enabled to act upon each other, the water itself taking no part other than that of a solvent."

PROFESSIONAL STATUS.—A Fellow has directed attention to a letter which appeared in the *Sydney Morning Herald* early in February commenting on announcements regarding vacancies under the Public Service Board: Head teacher blacksmithing—qualification, technical experience in the trade, salary £371; Head teacher, plumbing—qualification, expert knowledge of the trade, salary £340; Bio-chemist, Health Department—qualification, special training in bio-chemistry, Physiological chemistry, and immunology, must hold a university degree as Bachelor of Science—salary £298 15s. Under the *nom de plume* "Perplexed Parent," the writer of the letter comments on the circumstance that a man specially trained in three abstruse branches of science is offered a salary which the authorities do not dare to offer to a plumber, and shows good reason for hesitating whether to give his son a university training or to put him to plumbing. It is clear from the above that the Australian Chemical Institute and analogous organisations in the British Commonwealth must continue to co-operate actively in fostering among Government Departments a higher appreciation of science if the Empire is to reap the best advantage from its talent.—*Journal of the Institute of Chemistry*, June, 1921.

CHILIAN STATE RAILWAY REQUIREMENTS.—Tenders are invited by the Chilean State Railways up till 10 a.m. on August 31 next for the supply of emery and grindstones, bolts, nuts, cotter-pins, rivets, nails, and screws, telegraph and telephone apparatus, chemicals, &c. The estimated value of the material required is £44,000. Copies of the specifications (In Spanish) may be seen by United Kingdom manufacturers and exporters on application at the Enquiry Room of the Department of Overseas Trade, 35, Old Queen Street, Westminster, S.W.1. It is understood that the representative of the Chilian State Railways in Paris ((88, Boulevard St. Michel) has been instructed to obtain prices in the United Kingdom and remit same by cable on the day previous to the opening of tenders.

GENERATIVE REACTIONS OF MAGNESIUM.—The demands for magnesium during the war, directed the attention of M. Matignon to the question of

new methods for manufacture of this metal. He sought for an economic method, studying the three following reactions for this object: (1) $MgCl_2\ \text{sol} + C_2Ca\ \text{sol} = CaO\ \text{sol} + 2C\ \text{sol} + Mg\ \text{sol} + 22{\cdot}4$ cal.; (2) $MgO\ \text{sol} + C_2Ca\ \text{sol} = CaO\ \text{sol} + 2C + Mg\ \text{sol} - 8{\cdot}4$ cal.; (3) $MgOMgCl_2 + 2C_2Ca = CaOCaCl_2 + 4C + 2Mg\ \text{sol} + 1$ cal. $1 \times 2$; in which all the bodies are refractory, except magnesium and chloride of magnesium, the latter having, however, a very high boiling point, and resisting high temperatures without rapid volatilisation. — *Comptes Rendus*, 1921.

## NEW COMPANIES.

CLAPHAM DRUG STORES, LIMITED.—(175590)—Registered 7th July, 1921. 137, Landor Road, S W.9. To carry on the business of Chemists and Druggists Nominal Capital: £2,000 in 2,000 Shares of £1 each. Directors: T. C. Laws, 10, Lynette Avenue, Clapham, S.W.4.: (Governing Director). Qualification of Directors. £10 Governing Director 250 Shares. Remuneration of Directors To be voted by Company in General Meeting

A. W. HOCKIN, LIMITED —(175517).—Registered 2nd July, 1921. 133, Western Road, Hove, Sussex. To acquire and carry on the business of Chemists and Druggists Nominal Capital: £1,500 in 1,500 Shares of £1 each Directors · A. W. Hockin, 63, London Road, Brighton; J. Van Koert, 85, Montpelier Road, Brighton. Qualification of Directors · £100. Remuneration of Directors: To be voted by Company in General Meeting.

## New Patents.

THIS List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W.C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

17701—Adler, R —Manufacture of decolorizing charcoal of high activity. June 29.

17499—Carteret, G.—Preparation and purification of titanium compounds. June 27.

17661—Ellis, G. H.—Dyeing or colouring acetyl cellulose. June 29.

17833—Hormann, L —Manufacture of acid anhydrides. June 30.

17619—Howe, B.—Production of jink oxide or blown oxides from jink ores or products. June 28.

17810—Schwargkopf, R.—Method of manufacture of raw alkali-cellulose for working into viscose. June 30.

*Specifications published this Week.*

138113—Byrness, C. P.—Process of making aldehyde, fatty acids and aldehydes from mineral oils and their distillates.

140060—Duparc, L. and Urfer, C.—Process for the synthetic production of ammonia.

165144—Jones, F. B., Bury E and Minerals Separation, Ltd.—Flotation treatment of carbonaceous matter.

165167—Trotter, J. W —Process for the production of gasoline from kerosine and like hydrocarbon oils

148392—Schwabe & Co.—Process for the production of smoke on the stage by means of ammonium compounds of volatile acids

148885—Casale, L —Process for preparing nitrogen or nitrogen and hydrogen mixtures

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

## NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemical Apparatus, &c., for review or notice to be addressed to the EDITOR.

**SUBSCRIPTIONS,** £1 12s per annum, payable in advance, should be addressed to the MANAGER.

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THE CHEMICAL NEWS.

VOL. CXXIII, No. 3198.

## THE ASSOCIATION OF BRITISH CHEMICAL MANUFACTURERS

THE Fifth Annual General Meeting of the Association of British Chemical Manufacturers was held at the Chemical Society's Rooms, Burlington House, Piccadilly, W.1, on Thursday, July 14, 1921, for the purpose of receiving the Reports of the Council and of the Scrutineers, and for the election of the Auditors. SIR JOHN BRUNNER, Bart., Chairman of the Association, presided.

After the notice convening the meeting had been read, the Chairman in moving the adoption of the Report, said: We have now been working as an Association for five years, and I think that to-day is a critical point in the history of the Association. We have got over the first fine flush of our enthusiasm, and we are not yet respectable by reason of old age, not settled in our policy; so that it is a critical period. Our influence, gentlemen, is great, and it is growing. Hitherto there has been no association of chemical manufacturers to which the Government, or any other body, could appeal. Now they appeal to the Association of British Chemical Manufacturers as a matter of course. There were, of course, a large number of scientific societies connected with chemistry and chemical enterprise, but this association, I believe, in the hackneyed phrase, fills a long-felt want, and I believe for that reason that we will go on and prosper. The year has been a very active one in Parliamentary work. There have been three Bills. the Dyestuffs Bill, the Safeguarding of Industries Bill, and the Railways Bill, which have all occupied the attention of your Executive. The Dyestuffs Bill has now become an Act; the other two are not yet through. The Act, of course, concerns dyestuff makers and users, and to my mind if you are going to have protective legislation, that Dyestuffs Act is the fairest way in which you can arrange such matters, because the Committee which settles questions arising under the Act is composed of both manufacturers and users. Although things have not been perfectly smooth upon that Committee, I think the difficulties are gradually being solved, the friction is being avoided, and the scheme is going to work.

With regard to the Safeguarding of Industries Bill, that is now before the House, and, as you know very well, has been closured very severely. The third great piece of Parliamentary work that has been done by your Association is in connection with the Railways Bill. There has been, as you know, an Advisory Committee on this question which has met a very large number of times and reported to the Executive every month. The Railways Bill is now going through the House of Commons split up between two Committees. This Railways Bill is an extremely important thing for the whole trade of the country, and no less to chemical manufacturers. We hope to get something out of the Bill as it stands, but when the whole of the Bill is through the House, and has become an Act, then will begin the real work in dealing with the details of the rates. If anybody at a Board Meeting asks the representative of his particular company on the Association what the Association is doing for the benefit of that company, there is one thing which I wish you would say straight out in answer: we are looking after the Railways Bill; that is to say; we are looking after railway rates on your behalf. If we were doing nothing else, gentlemen, that would justify the existence of the Association.

Then with regard to the other activities of the Association, we have been very busy in administrative matters, quite apart from legislative matters. The Smoke and Noxious Vapours Abatement Departmental Committee was attended on our behalf by Mr. Max Muspratt, and he gave advice, which I think is very good, to that Committee, namely, that they should work on the lines of the Alkali Act. That Act was originally I believe, very much objected to by the alkaline manufacturers, but in the long run they have found that the alkali inspectors have rather been of assistance to them in their work than otherwise If the Committee continue their work and a Bill is in the future founded upon the same lines I think the chemical manufacturers of the country will have nothing to fear It is the duty of all of us—and I am quite sure everybody agrees with me—to try and stop the smoke and noxious vapours nuisance. The experience of those who have lived in London during the last three months, when it has really been quite a pleasant place to live in on account of the absence of smoke, will go to show that it is the duty of the chemical manufacturers of the country to do all they possibly can to purify the atmosphere of our big towns. (Hear Hear.) Then with regard to the Home Office Regulations under the Factory and Workshops Act. The Association ought to raise the strongest protest of which it is capable against the procedure of the Home Office in this matter. As you very well know, legislation is passed now-a-days simply because the mass of it is so large that Parliament cannot attend to all the details, giving powers to Departments to make regulations which have the force of law. The Home Office actually has the power, without appeal, to prohibit any chemical process. They could to-day send an inspector to your works and say that you must not continue a certain process. I do not suppose they would venture to do such a thing as that, but they actually have the power. They have, as you know, issued certain regulations for what they term the dangerous and unhealthy parts of our business. We have been able to somewhat mitigate the effect of those draft regulations; the matter is still under negotiation, and although we shall not get any satisfaction, yet we shall not be subjected to the dangerous, so far as our businesses are concerned, parts of those regulations.

We have in the past and previous years encouraged research in many ways, and have given a substantial contribution to the Chemical Society's library.

The Joint Research Committee of the Association and of the British Chemical Plant Manufacturers' Association has been continuing its work, and I believe that it will succeed in standardising many types of plant and thus make it very much cheaper for manufacturers. It has often been a

reproach to British industry that there is so little standardisation I believe that this Research Committee will, in the course of time, very much cheapen our plant Then further, we have to foster the production of research chemicals. We have obtained information as to what research chemicals are made in this country, and suggested to people that those which are lacking should be made by somebody. We have in these ways and in many other ways suggested to members that they should co-operate. It is, of course, a very difficult thing to get people to co-operate who are competitors in business. They have been very individualistic in the past, but there are so many ways in which they can co-operate to their mutual benefit, that this Association, I think you will agree, is doing right in endeavouring to get them to co-operate in those ways which are to their mutual advantage. (Hear Hear.) This co-operation has, as I say, taken the form of the stimulation of production of dyes and other fine chemicals, by the provision of the proper intermediates and raw materials by members of the Association. We have further co-operated by endeavouring to put the members into touch with anybody who is anxious to get certain materials and have endeavoured to find out where such materials can be acquired, and having done so we have brought together the supplier and the man requiring the particular article.

On the whole, I think you can congratulate yourselves upon having had a very successful year as an Association. We are all now going through very bad times, and my only wish for all the members of the Association is that we are now at the bottom, and that trade and industry will begin from now to rise to a pinnacle of prosperity. (Cheers.)

Dr. E F. ARMSTRONG, F.R.S., in seconding the motion for the adoption of the Report, said that to the majority of members of the Association the fact that the Dyestuffs Bill passed through the House, and that the Safeguarding of Industries Bill was very nearly in the same position, would be regarded as the most important events of the year. From the point of view of the chemical trade he thought they ought not to overlook two points, that whilst they had asked the Government to help to safeguard their industries during the critical period which lies ahead, they must not in any way relax their own efforts to make themselves independent of the Government. (Hear hear.) That is the first point. The second point was that this assistance from the Government would be all too dearly bought if it involved too much Government interference. (Hear hear.) His third point was the delay—so dear to the heart of the bureacrats, but the greatest enemy of trade —an if as a result of any of this new legislation they were not able to get the goods they wanted, and had to suffer those irritating delays, then it would be a great handicap. With regard to the publication of the list of research chemicals, he thought in time it would become a very valuable document, and one of which they would all be proud, and which would certainly lead to efforts being made to increase the number of those compounds valuable for research, and so emancipate them from any Continental influence. More particularly, he would like to refer to the very valuable work done in connection with chemical plant. In the old days a chemical manufacturer in this country wishing for plant had either to go to a local foundry with his own design and get it made, and then find out that it would not work, and thus be unable to profit by previous experience of others, or he had to go abroad, put himself in the hands of the Germans, and take what they chose to sell him—generally, he admitted, with satisfactory results—or he had to go to some of the few chemical plant manufacturers here and pay rather dearly for his plant, and again find that he only got to a limited extent the advantage of the experience of others. They wanted to change all that, and he thought they were beginning to change it. He was certain that the Joint Research Committee was a valuable first step in that direction.

The Treasurer, Sir WILLAAM PEARCE, M P., commented on the statement of accounts, and congratulated the Association on its financial position. He also referred to the present position of the Railways Bill, and stated that he would like the meeting to say if it was of fundamental importance to the industry that the Bill should go through or could they look with a certain amount of equanimity if it was held up for the time being? The House of Commons might have to make up its mind very seriously whether it would struggle to get the Bill through or whether it could be be allowed to drop and be brought up at a more convenient time. It did appear to him that if the Railways Bill were held up, at any rate, the agreement with the railway companies would have to go through, and they would then have to lose one of their great holds on the railway companies, because the payment by the State of 60 million pounds, less certain allowances, was conditional on their granting certain securities as to profits. He did not see how the financial agreement could be held up, because the position of the railway companies would be such that unless a settlement was arrived at, their debenture interest and preference dividends and many other things would be in jeopardy, because this money was owed them by the Government.

The General Manager, Mr. W. J. U. WOOLCOCK, C B.E., M.P., said there had been a rather serious disagreement on the question of exceptional rates. The railway companies held very strong opinions on the clauses in the Bill, and after listening to their case, he came to the conclusion that they had an almost unanswerable case; not purely from the argumentative point of view, but what was even stronger than mere argument, namely, the physical impossibility of carrying out the suggestions of the Government. The clauses as they stood would be unworkable. He thought it was physically impossible in the time allowed, to adjust the enormous number of exceptional rates, and therefore, the Government were bound to meet them on the point.

Mr. KENNETH CHANCE, M.A., dealt with the standardisation of chemical plant. With regard to the Railways Bill, he thought that if its passing meant a strengthening of Government control, and probably the continuation of one of the Ministries, by all means let the Bill go. They could settle things very quickly amongst themselves; the railway directors and their managers had ample opportunities of seeing the advantage of co-operation one with the other during the war,

and they knew infinitely better than the Minister of Transport how far that co-operation could usefully be carried out.

Dr. P. C. C. Isherwood said that up to the time of the Dyestuffs Bill being introduced into the House of Commons they all thought that fine chemicals would be incorporated in that Bill, and he thought they would have been very much better pleased to have had fine chemicals included in that Bill than in the present Bill. The last thing that fine chemical manufacturers wanted was to adopt a check on manufacturing output. They wanted to give the freest opportunity for users in this country, particularly those who are connected with the export trade, to freely export anything which they could not, or had no prospect of manufacturing.

Mr. E. V. Evans, O.B.E., F.I C., thought that the one great accomplishment of the year was the passage of the Dyestuffs Bill, and he congratulated the Association upon the part which it had played in its passage through the House. The Licensing Committee, formed to work the Act, was a body of men really keen to carry out the principles laid down, the main principle being that the dye industry of this country should be fostered without prejudicing the users' interests. He would like to pay a tribute to the attitude adopted by the users' representatives on that Committee There were many difficulties, but it would be readily imagined that the task of examining our British colours and of determining whether they are a suitable substitute to replace imported articles and then scheduling and pooling the information so that it can be used at a later stage, represented a fairly large scheme. He could assure them that the Committee was in no way satisfied that it had attained the ideal it set itself in this respect. There was already a vast amount of information collected, and it behoved them at this stage to take adequate advantage of the information that has accrued.

Mr. Thomas Morson thought that in view of the amount of spade work that has been done by members, the dropping of the Railways Bill would be a disaster.

The Rt. Hon. J. W. Wilson, M.P., said that the Railways Bill consisted of three parts: one to meet the question between the Government and the railways, and to avoid, by a definite Parliamentary settlement, possibly years of negotiation and law suits and legal questions which did nobody any good except the lawyers, that was the sum to be paid in satisfaction of the past war claims; secondly, to carry on some sort of agreed machinery for settling wages and salaries on the railways, which also vitally indirectly affected the public, because only by proper handling of that question could disastrous strikes be avoided on the one hand or rates cut down and the expenses of railways kept within limit. Those two he imagined the Government were sure to want to put through. The tendency had been, especially when a question arose as to dividing the Bill, that many Members of Parliament suggested that the rates question be left until another year, and of course, there was no doubt that the railways and the men would both acquiesce in that so long as they had their part of the settlement. He felt that as a body of traders they ought to make their views perfectly clear as to whether or not they would venture to defer the whole rates fixing machinery of the Bill till next year Personally, he felt that in all big settlements of great national questions when there are three distinct interests involved, traders, railway shareholders, and men, that it was from a statesman's point of view and a general welfare point of view very much easier to get a fair settlement if they were all done at once than when one of the interests was left out. (Hear hear)

Mr. Max Muspratt, J.P., felt that it was better to have a bad Railways Bill than none at the present time. It was always possible to have things improved afterwards. After all, the work that has been done it would be highly undesirable to say that in the main it should be held over. With regard to the Safeguarding of Industries Bill and the Dyestuffs Act, he agreed that ultimately the only protection was sound manufacture, and there they could do a very great deal by following up their ideas of co-operation. The Dyestuffs Act would be more or less futile if they did not believe that it was going to lead to a great deal more co-operation and delimitation. In the much more intricate problems of fine chemicals they would have to survey the ground of the whole fine chemical industry and find out what was best to be done.

Mr. Thomas Horrocks also spoke on the Railways Bill, and

Mr. Richard Seligman on the Joint Research Committee work.

The Chairman replied to the points raised in the Discussion. The Report was then unanimously adopted.

The following Resolution was carried:—

"That this meeting is of the opinion that it would be unfortunate if any of the parts of the Railways Bill were dropped, and urges the Government to take every possible step to secure the passing of the Bill."

On the motion of Sir William Pearce, seconded by Mr Muspratt, the Auditors, Messrs. Feasey & Co., were unanimously re-elected.

The report of the Scrutineers was received and adopted.

Mr. R. G. Perry, C.B.E., proposed a hearty vote of thanks to the Chairman, which was carried with applause, and the Chairman returned thanks. The proceedings then terminated.

The Rt Hon. J. W. Wilson, M.P., has been appointed Hon. President in succession to Lord Moulton. Mr. R. G. Perry remains the Hon Vice-President. Sir John Brunner continues in office for a second year as Chairman, and Mr. Max Muspratt succeeds Dr. E. F. Armstrong as Vice-Chairman. Sir William Pearce, M P., continues as Hon. Treasurer.

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The French Monthly Review *Arts et Métieres*, which was discontinued during the war, is again published. We have received the May number, which contains much interesting matter. The Journal is published by J. Loubart, 15, Boulevard St. Martin, Paris; price 3 francs per number.

The office of the Australian Institute of Science and Industry has been removed to 314, Albert Street, East Melbourne.

# THEORY OF MOLECULAR REFRACTIONS.

## Part II.—Free and Activated Valencies.

By GERVAISE Le BAS, B Sc

### *Note on Molecular Refraction and Valency.*

The following group relationships are to be noted :—

| | F. | Cl. | Br. | I | Na. |
|---|---|---|---|---|---|
| | 0·67 | 5·96 | 8·79 | 13·87 | 2·56 |
| Δ | | 5·29 | 8·12 | 13·20 | |
| | | 2×2·65 | 3×2·70 | 5×2·64 | |

2·65=4×0·67.

| | O. | S. | Se. |
|---|---|---|---|
| | 1·48 | 7·76 | 10·84 |
| | | 6·28 | 9·36 |
| | | 2×3·14 | 3×3·12 |

3·14=4×0·78 and 2×1·57.

It seems evident that a greater fraction of the atom affects the molecular refraction in one case than the other. (1) It is seen that there is a common factor in the different groups which is not the same for each group. (2) This seems to be related to the complexity of the elements and their genetic relations.

### *Free Carbon Valencies.*

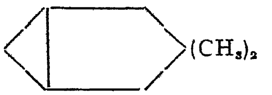
The molecular heats of combustion of unsaturated compounds show that the ethenoid and acetylenic linkages are weak, and that consequently a large amount of unsaturation exists. This *involves* the existence of free valencies. These conditions can be shown to exist by means of the molecular refractions.

Ethylene. Acetylene.

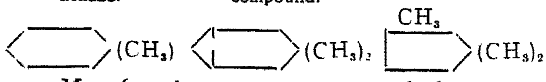
| | Ethylene | Acetylene |
|---|---|---|
| Δ | 1·56 | 2·12 |
| | 2×0·52 | 4×0·53 |
| | +2×0·26 | |

The anomaly for a free valency is 0·52 The substitution of unsaturated carbon gives rise to an anomaly of 0·28 as for · C—$CH_3$. This substitution anomaly is lost in acetylene owing to compensation or neutralisation.

A proof that the valencies are free is found in an unique compound discovered by Zelinsky and Utskensky, and which was misnamed 3 : 3-dimethyl 0 : 1 3-bicyclinonane.



1:1 dimethyl cyclo hexane. Zelinsky and Ulskinsky's compound.



| | | | |
|---|---|---|---|
| $M_x$ | 36·47 | 35·95 | 36·96 |
| Δ | 1·57 | +1·02 | 0·04 |
| | | 2×0·51 | |

### *Molecular Volumes.*

Monocyclic Molecular Volumes

| | | | |
|---|---|---|---|
| $V_{b\,p}$ | 153·4 | 153·6 | 163·3 |
| Δ | −16·8 | −16·6 | −14·6 |

It is thus seen that the compound in question possesses two free valencies, otherwise shown by the monocylic structure.

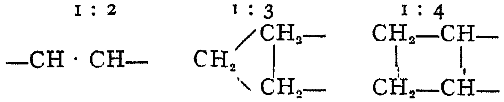
It is thus seen that free valencies can exist and are shown by the molecular refractivities. They give rise to an anomaly of 0·52.

This structure is intermediate between the ordinary 1 : 2 unsaturation and the ordinary bridged ring which may show an anomaly of 0·67 or 0·26, as in the case of some terpenes.. Part of the anomaly in the first case is due to substitution (2×0·28) $C_p$ benzene substitution by $CH_3$.

### *Anomalies Due to Unsaturation.*

*Unsaturated Combinations* :—

1 : 2 1 : 3 1 : 4 1 : 5

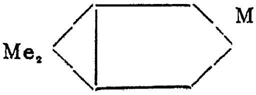


| | 1 : 2 | 1 : 3 | 1 : 4 | 1 : 5 |
|---|---|---|---|---|
| Δ | 1·56 | 0·68 | 0·48 | 0 |

(Hans T Clarke).

The unsaturation of the bridged ring thus amounts to 0·68, as follows ·—

2 : 6 : 6 trimethyl 0 : 1 · 3 bicyclonane (N. M. Kishner).

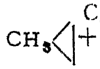


$M_\alpha$ 40·21 Δ+0·82

Molecular volume

$V_{b\cdot p}$ 157·6 Δ —20 { 14 5 / 5 5

1 methyl 2 isopropyl cyclopropane



$M_\alpha$ 37·57 Δ+0·51

$V_{b\cdot p}$ 170·2 Δ 7·6

Zelinsky and Utskensky have thus discovered an unique compound which diverges from the bridged ring type, which is monocyclic, and possesses two free valencies.

### *Free Valencies in Sulphur.*

The amount of activation of the supplementary valencies so far, has been shown to be 2×0·26 as for the diselenides. The Xanthates and allied compounds show many such cases. The local anomaly is, however, dependent on the general unsaturation.

It should be noted in the first place that the A. R of doubly-bound sulphur is $r_\alpha$ 9·07 Δ= 9·07−7·96=1·11 (2×0·56).

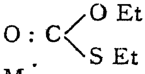
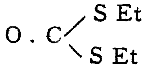
or C=S<

probably the latter, since C ⁝ N shows no anomaly. Nitrogen, more difficult to activate in this way than a heavier atom, is like sulphur. Various values of sulphur are found in the Xanthates, which involve activated or free valencies.

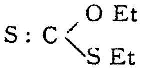
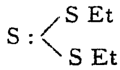
| | >S 1 | > $S_2$ | · S |
|---|---|---|---|
| | 7·96 | 8·20 | 9·06 |
| | | 7·96 | 7·96 |
| Δ | | 0·24 | 1·10 |
| | | 2×0·12 | 2×0·55 |

The first is a partial activation; the second is complete. Many cases exist which illustrate the rule of mutual interaction or influence resulting

in partial activation of the supplementary valencies.

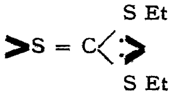
 

| | | |
|---|---|---|
| $M_\alpha$ | 34·90 | 41·88 |
| $Enr_\alpha$ | 34·74 | 41·12 |
| $\Delta$ | +0·16 | 0·76 |

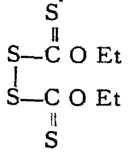
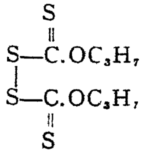
| | |
|---|---|
| 41·52 | 48·47 |
| 42·13 | 50·03 |
| 0·16 | 1·56 (2×0·78) |

The degree of activation thus depends upon the contiguity of two sulphur atoms, and increases with the number. The influence which causes these effects is no doubt cumulative, but the activation is that of the ethereal sulphur atoms. The value 0·76 is equal to half the anomaly for an ethereal link and 1·56 the full anomaly. One might thus represent the linkage between the two contiguous sulphur atoms by



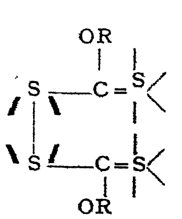
Cross ethenoid unsaturation.

Another case which shows an analogy between unsaturated sulphur and carbon is that of the dioxysulphocarboxylic esters.

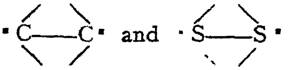
 

| | | | |
|---|---|---|---|
| $M_\alpha$ | 67·09 | | 76·46 |
| | | Previous compound | 67·09 |
| $C_7H_{10}$ | 20·44 | $2CH_2$ | 9·16 |
| 2C | 4·96 | | 76·25 |
| 2O | 3·24 | | |
| 2S | 18·04 | | |
| 2S | 15·92 | | |
| | 62·60 | | |
| | 67·09 | | |
| | +4·49 | | |
| | 4×1·12 | | |
| | 8×0·56 (free valencies) | | |

It must be assumed that there are four pairs of free valencies in addition to the two belonging to doubly-bound sulphur. The formula would thus be :—



This remarkable case shows a sulphur atom with four activated valencies, and also a combination similar to acetylene. One thus finds

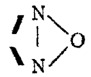


It should be stated that the great activation is possible by the continuous chain of unsaturated atoms and the requisite number of supplementary valencies.

*Conclusions.*—The tetravalent and hexavalent functions of sulphur are shown by the foregoing as for carbon, although part of the valencies are uncombined. Similar types of unsaturation is found in sulphur as in carbon combinations with one which is characteristic of sulphur.

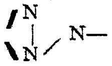
## *Nitrogen.*

Nitrous oxide



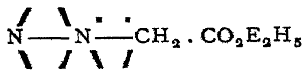
| | |
|---|---|
| $M_\alpha$ | 7·58 (gas) |
| 2N | 4·96 |
| O | 1·62 |
| M | 7·58 |
| $Enr_\alpha$ | 6·58 |
| | +1·00 (2×0·50) |

The value for the triazo group $N_3$ is 8·96.



| | |
|---|---|
| $N^{III}$ | 2·90 |
| 2N | 4·96 |
| $\Sigma nr_\alpha$ | 7·86 |
| $M_\alpha$ | 8·96 |
| | +1·10 (2×0·55) |

Curtis' compound diazo ethyl acetate is especially interesting. The anomaly is made up from 1·56+2·12=3·68, equivalent to an acetylene and ethenoid combination. The formula is :—



A complete parallelism has thus been found between carbon sulphur and nitrogen as regards the relation between unsaturation and the Molecular Refraction. Seeing that the atoms are different, there is no reason why similar numerical relations should be obtained unless the unsaturation were caused by some common circumstance not dependent upon the nature of the atom. This is unmistakable evidence for an electronic condition which is that of the unsaturated centres just stated. Electrons may be supposed to be pushed out or at least occupy positions in the absence of hydrogen which allows of retardation of the light. This side of the question is now receiving attention in England and America.

It must not be lost sight of that two overlapping conditions—the material and the electrical—exist, and it is sometimes doubtful whether the anomalies represent free valencies or not, *c.p.* anthracene and acridene. They may, however, be supposed to be free in most cases. Anomalies not connected with valencies also exist as for conjugations

—CH : CH •—• CH : CH—

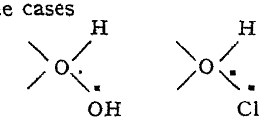
We may thus distinguish ***Fundamental Anomalies*** or unsaturation—that is where free valencies are

concerned. *Derived or Induced Unsaturation* for conjugations (2) and substitutions (1).

It may thus be concluded that molecular refractions are due to the light arresting or scattering power (dispersive) of valency or electronic conditions, first by the atom itself, secondly, by the free valencies [separated electrons], thirdly, by the induced electrical condition. It seems that in any electronic theory, account must be taken of the molecular refractions, and on the other hand, an adequate explanation of these must follow along the lines of an electronic theory. The writer is disposed to view the valency conditions of an atom as regional and of involving definite fractions of the atomic spaces, that is, the valency condition is such as to involve a definite fraction of the circumscribing spherical surface, and extends to the interior. Thus many electrons may be involved in the valency as a region.

It is thus to be seen that a very great extension of Eisenlohr's theory of activated supplementary valencies has been made. Only the exigencies of space have prevented the writer going into detail.

*Note.*—The cases



$\Delta + 1{\cdot}54$ have been referred to.

*Negative Anomalies.*

The cases of $(CH_3)_3C.CH_2Br$, $(CH_3)_3\,C.CHBr$ have already been referred to.

Similarly thiophene and furfural have been noted (*Trans. Farad. Soc.*). Pyrrol does not show a negative anomaly, a fact which seems to be due to the presence of a positive hydrogen. For a similar reason the $CH_3$ group shows little disturbance.

*Sulphur.*

It has been found that oxygen is especially liable to show a negative anomaly which frequently practically gets rid of the atomic refraction.

| | $M_a$ | $\Sigma nr_a$ | $\Delta$ |
|---|---|---|---|
| $O{:}S(OEt)_2$ | 31·62 | 33·60 | −1·98 |
| $O_2{>}S(OEt)_2$ | 31·79 | 35·7 | −3·92 |
| | | | 2×1·96 |

$O^{11} = 2{\cdot}12$ normally $2{\cdot}12 - 1{\cdot}98 = 0{\cdot}14$

*Selenium.*

| | | | |
|---|---|---|---|
| $(HO)_2{>}Se\ O$ | 15·71 | | −2·61 |
| | | $O_1$ | −0·60 |
| | | $O^1{}_2$ | −2·00 |
| $(HO)_2{>}Se{<}O_2$ | 17·21 | −3·21 | |
| | | : O | −1·20 |

*Phosphorus* P 7·69

| | | | |
|---|---|---|---|
| $P(OEt)_3$ | 38·30 | 43·24 | −4·94 |
| | | | 3×1·64 |
| $O:P(OEt)_3$ | 41·49 | 45·48 | −4·99 |
| | | | 3×1·66 |
| $C_6H_5$—P(OH)(OH) . O | 35·61 | 40·18 | −4·57 |
| | | | 3×1·52 |

| $O:P{<}Cl_2$ | $S:P{<}Cl_2$ |
|---|---|
| 25·24 | 33·48 |
| 27·72 | 34·50 |
| −2·44 | −1·02 |

Sulphur seems less susceptible to negative anomalies than oxygen. These cases are sufficiently remarkable to form the basis of a collection of data from which cases of negative anomalies may be drawn.

The fact remains that light is not only not impeded by the passage of the light waves, but accelerated, relatively speaking. The cause of the negative anomaly is unknown, but the waves $H_\alpha$ pass as if the O atoms did not exist. It would be interesting to ascertain what would be the effect if shorter and probably more penetrating waves like $H_\beta$, $H_\gamma$, were used.

## ATOMIC WEIGHT OF GERMANIUM.*

By JOHN H. MÜLLER.

IT is recognised that the atomic weight of germanium is not accurately known, the accepted value being entirely dependent upon the investigations of its discoverer (*J. prakt Chem.*, 1886, [2] xxxiv., 177. Aside from the lack of confirmation of this constant on the part of other workers, it should be noted that Winkler's determinations were made very shortly after his discovery of the element, so that the time interval between the announcement of the existence of the new element and the determination of its atomic weight could not have permitted the determination of special means of purification to which germanium compounds may now be subjected.

The purpose of this investigation was to develop a more thorough means of purification of germanium compounds, especially in connection with the elimination of tin, arsenic, and silica, with which germanium is always associated, and to use the purified product for a redetermination of this much-neglected constant.

Winkler decomposed the tetrachloride by sodium carbonate, added an excess of standardised silver solution and titrated back the excess of the latter with ammonium thiocyanate solution. Four determinations were recorded. Winkler's reasons for the use of the Volhard method are interesting, namely, that the silver chloride which he precipitated after decomposition of the tetrachloride could not be determined gravimetrically on account of occlusion of germanic acid in the precipitated silver chloride. His effort to oxidise the disulphide with nitric acid and to precipitate the equivalent of sulphuric acid as barium sulphate also met with failure for the same reason.

Thus it is not possible to determine halogen or sulphuric acid accurately in a solution con-

*From *Journal of the American Chemical Society*, May 1921.

taining germanic acid by the usual gravimetric procedure.

This behaviour on the part of aqueous solutions of germanic oxide is analogous to the occlusion of stannic acid when the corresponding tetrachloride and sulphide of tin are treated in the same manner.

The brevity of the literature of germanium at this date is doubtless due to the great rarity of the element which until 1915-16 was not known to exist in other than a few scarce minerals, argyrodite, in which it was first found, and certain canfieldite-argyrodite mixtures.

Urbain states that Winkler's original source of germanium was not really argyrodite but mixed minerals containing much less than the theoretical 70 per cent of germanium present in the pure mineral *Compt. Rend.*, 1910, cl., 1758). Hillebrand and Scherrer in their work on gallium in spelter, mention the existence of germanium in a number of blends, as shown spectroscopically by K. Burns of the U.S. Bureau of Standards (Hillebrand and Scherrer, *J. Ind. Eng. Chem.*, 1916, viii., 225).

The same element has been reported in euxenite to the extent of 0·1 per cent (Krüss, *Ber.*, 1888, xxi., 131; *ibid.*, 1887, xx., 1665), and has been reported and also denied to be present in tantalite, samarskite, fergusonite, and some other allied minerals.

The writer has examined large quantities of Swedish samarskite, euxenite, aeschinite, and gadolinite and failed to find any germanium in these with the exception of a single sample of euxenite which contained 0·03 per cent. All of these minerals were decomposed by alkali carbonate fusion, the melts converted to chlorides, and these subjected to the hydrochloric acid and chlorine distillation method for germanium.

Argyrodite is very scarce and since its discovery in Freiberg ore in 1885 has been reported in only a few localities, notably in the silver ores of Oruro, Bolivia. Hence the recent discovery of workable quantities of germanium in the zinc oxide residues of the spelter industry, is most interesting and important. Certain of these residues contain as much as 0·25 per cent of germanium dioxide (Buchanan, *J. Ind. Eng. Chem.*, 1917, ix., 661).

Through the courtesy of the New Jersey Zinc Company, a quantity of this crude zinc oxide was procured, from which nearly all the germanium compounds used in this investigation were prepared.

The oxide-to-metal ratio for the atomic weight of germanium was tried by Winkler but was abandoned as unsatisfactory. Aside from difficulty in preventing enclosure of oxide in the reduced metal, Winkler did not mention specific reasons for his failure to obtain good results. An attempt was made to redetermine this ratio using specially constructed quartz apparatus so arranged as to prevent loss of metal by volatilisation. Results were very unsatisfactory for two reasons. First, the purity of the oxide was questionable for traces of sulphur were contained in it (when prepared from the sulphide) and small amounts of chlorine (when prepared from the tetrachloride) were not eliminated. Second, the hydrogen stream carried away small quantities of metal as hydride. This was proved by washing the waste hydrogen in a solution of silver salt, when a small black deposit was slowly formed which contained silver germanide and metallic silver.

It was noted, however, that the reduction to metal proceeded to completion at 700°, *i.e.*, 200° lower than the melting-point of the metal. Every reheating in hydrogen at this temperature, however, caused further loss in weight.

The chief difficulties in determining the chlorine in the tetrachloride, or halogen in the other halides, are twofold; the occlusion of germanic acid in the precipitated halide previously mentioned, and the instability of the halide of germanium in air and the elaborate method required for the preparation and preservation of this group of salts.

The writer examined the properties of potassium fluogermanate and found that the stability and definite character of this salt strongly recommend it in what appears to be a simple and satisfactory ratio, namely, the conversion of this compound to potassium chloride in hydrogen chloride. The ratio of potassium fluogermanate to potassium chloride offers certain important advantages. The complex salt contains no water of crystallisation, and the dried product is remarkably non-hygroscopic. It is sufficiently stable and non-volatile to withstand the action of heat at 400° to 500° without loss of weight.

The fluogermanate melts at about 730° to a clear liquid, and at about 835° rapidly vaporises without change The salt is slightly volatile in an air current below its melting point—as might be expected, but as a much lower temperature could be used for its conversion to chloride no difficulty was encountered in this direction.

The decomposition of the double fluoride in hydrochloric acid was shown by preliminary experiments to be complete at a temperature well below 400° and in the presence of water was completed at about 100°. That is to say, tests for germanium and fluorine in the residual chloride gave entirely negative results in these cases. Concerning the final product, potassium chloride, the work of Richards on the atomic weight of potassium (Richards and Staehler, *Jour. Am. Chem. Soc.*, 1907 xxix., 623), has already shown that this salt may be weighed with great accuracy. Finally, the method outlined was free from complicated manipulation, and required no transference of material after placing the original sample of fluogermanate within the weighed platinum bulb.

*Preparation of Material.*

Twenty-nine kg. of germanium-bearing zinc oxide was slowly sifted into conc. commercial "C.P." hydrochloric acid (sp. gr. 1·18). Solution was nearly complete, and on cooling large masses of lead chloride crystallised out, yielding in all 3 kg. The filtrate (which measured about 65 litres) was placed in 5-gallon carboys and saturated with hydrogen sulphide under pressure. The calculated excess of hydrochloric acid present was such that the precipitate contained little else than the crude sulphides of arsenic and germanium. Siphon fillers were used to remove most of the filtrate, and the sulphides were collected in large Büchner funnels upon which they were washed and sucked as dry as possible The sulphides were then dissolved in a very slight excess of dil. ammonium hydroxide. The thio salts obtained

were strongly acidified with hydrochloric acid, and the sulphides were reprecipitated with hydrogen sulphide, after which they were washed and dried, roasted in air in quartz vessels, and digested, with frequent addition of pure nitric acid. Ignition gave a snow-white voluminous residue of crude germanium dioxide which weighed approximately 50 g.

This oxide was introduced into a large distilling bulb, together with 20 per cent hydrochloric acid, a quartz condenser was attached, and the whole system was filled with chlorine to saturation in the cold. Distillation was then carried out in a stream of chlorine and the distillate caught in a receiver containing cold water. The distillation was repeated four times. The final distillate was then saturated with hydrogen sulphide prepared from selected pure antimony trisulphide. The snow-white germanium sulphide thus obtained was treated in quartz dishes with pure freshly-distilled nitric acid, gradually brought to dryness, and ignited. Treatment with nitric acid and subsequent ignition was repeated many times. The strongly ignited residue of oxide finally obtained weighed approximately 46 g.

The oxide was then placed in freshly distilled water contained in 3-litre Erlenmeyer flasks of well-seasoned resistance glass, the mixture stirred by a current of washed air until most of the oxide had dissolved. Warming was avoided on account of possible reaction with the glass surface. 12 litres of aqueous solution and a residue of undissolved oxide were obtained. The perfectly clear supernatant liquid was removed through a syphon filter and the residual oxide, amounting to about 3·5 g., discarded.

Later examination of this residue showed that it was nearly completely soluble in water Several mgrms. of a white insoluble powder remained, however, which required alkali-carbonate fusion for decomposition. Indistinct tests for sulphur and silica were obtained, but lack of sufficient material prevented an exact determination of its nature.

The large volume of aqueous solution was evaporated in quartz vessels enclosed in bell jars. The dishes rested upon steam-heated copper coils, and a current of washed warm air was drawn through the system to remove water vapour. The first deposit of hydrated germanic oxide (3·4 g.) was removed by filtration and set aside. Evaporation was then continued until most of the oxide had crystallised. Slightly over a litre of mother liquor was set aside, and the middle portions of hydrated oxide deposited were filtered out, washed with a little cold water, and finally strongly ignited in platinum. 37·1 g was obtained The fluogermanate of potassium was now prepared from this fraction of oxide.

*Potassium Fluogermanate.*—The purest obtainable commercial potassium nitrate was recrystallised in platinum five times with centrifugal draining, then fractionally precipitated as chloride in quartz vessels by a stream of hydrogen chloride. The chloride was reprecipitated three times by hydrogen chloride, and the resulting chloride then converted to the acid tartrate, using tartaric acid which had been recrystallised until no weighable residue remained upon ignition of a 5 g. sample. The bitartrate after three reprecipitations was centrifuged in platinum cones and finally ignited to the carbonate in a platinum dish. Cesium, rubidium, and sodium could not be detected spectroscopically in this potassium carbonate.

Hydrofluoric acid was prepared, starting with the best commercial "C.P." acid. The common impurities in this acid are silica, lead, iron, chlorine, and organic matter. Precipitation to eliminate any of these possibly present was carried out as follows. Potassium carbonate, prepared as described above, was added to the hydrofluoric acid, but no visible trace of any precipitate was found. The acid was then filtered through paper which had been thoroughly washed with a portion of the acid, and potassium fluoride was then added, the acid distilled from a platinum retort and condenser, and redistilled first in presence of a little permanaganate and then over a little pure silver fluoride, formed by adding a little silver carbonate to the acid. The resulting purified acid was then again distilled alone, and tested for non-volatile matter, but gave no weighable residue.

The pure germanium dioxide described above was warmed in a platinum dish with an excess of this acid until solution took place Very slightly more than the calculated amount of purified potassium carbonate was added to the hot, perfectly clear, acid solution of the fluoride. Precipitation of the double fluoride which began in the hot solution was made as complete as possible by chilling. The precipitate was filtered out upon platinum cones and centrifuged, washed with a little cold water, fractionated by crystallisation from hot water slightly acidified with hydrofluoric acid, recrystallised four times from hot water containing a little free acid, and finally again from water alone. Each fractionation was accompanied by thorough centrifuging of the crystals and because of the marked difference in solubility of the salt in hot and cold water, all filtrates were set aside without further concentration.

The pure white glistening crystals thus obtained were preserved in a platinum vessel over sulphuric acid in a dessicator whose inner surface was protected from the action of traces of hydrogen fluoride by a coat of Canada balsam.

*Reagents.*

*Water.*—Ordinary distilled water was redistilled from alkaline permanganate solution, then from acid permanaganate, and then alone. A block-tin condenser was employed, and the distillate was received in well-seasoned Jena glass flasks. Ground glass surfaces were avoided, the receiving flasks being provided with caps ground on the outside of their necks Spray from the still was eliminated by use of a bead-filled splash trap The first third portions of distillates were not used.

Small quantities of specially pure water were required from time to time, to be added to the weighing bulb wherein evaporation to dryness was effected. For this purpose water prepared as described above was again distilled from an all-platinum still and condenser, collected in a receiver of the same material, and used immediately.

*Hydrogen chloride* was prepared by the Hare method, using arsenic and iron-free concentrated hydrochloric and sulphuric acids. The gas was washed and dried in four sulphuric acid towers filled with beads and glass wool. The generator

connection was a ground glass joint and all other connections were sealed by fusion.

*Nitrogen* was required only for fusion of the potassium chloride previous to the estimation of that salt. The gas was purified by passing it through sulphuric acid, over fused potassium hydroxide sticks, finely divided hot copper, again over fused caustic potash and finally through phosphorus pentoxide. Fused glass connections were used throughout.

*Air.*—An air current produced by a water blast was purified by passing through a silver salt solution, alkaline permanganate solution, over caustic potash, through sulphuric acid towers, over fused caustic potash and soda lime, and finally through two towers containing phosphorus pentoxide. As in the case of the nitrogen and hydrogen chloride systems all connections were of sealed glass.

*Nitric acid* was prepared from a commercially obtained C.P potassium nitrate. The acid was redistilled thrice from an all-quartz apparatus; 10 cc. of the final distillate was free from non-volatile residue, and gave a negative test for chlorine and iron.

(To be continued)

## UNIVERSITIES, RESEARCH, AND BRAIN WASTE.*

By J. C. FIELDS, Ph.D., F.R.S.

(Continued from p. 48).

THE fundamental defect in the educational systems on the American continent is the failure to make adequate provision for the training of the exceptionally gifted. It is quite evident that funds must be provided for the care of the mentally defective. A proposition to help those who are backward in their studies will receive a sympathetic hearing. If, however, it were proposed that the State should spend money in establishing a school for genius after the model of one or other of those which are supported by the State in France, the cry of class privilege would be raised If there were question of extending financial aid in their studies to one or other of two boys, the first of whom was exceptionally gifted, the second of mediocre capacity, and if the man on the street were consulted in the matter, he would more likely than not advise that the money be given to the second boy on the ground that he was already handicapped in competition with the first boy

With France, we should learn to realise that the exceptionally gifted individual is there for the good of the community. All the ameliorations which we enjoy we owe in the last resort to such individuals. The State, then, may well defray the cost of their training for it will ultimately profit more from the expenditure than those on whom the money is expended. One creative worker who adds an increment to the heritage handed down from generation to generation ultimately means more to the nation and the race than a hundred mediocrities trained to their capacity. No number of trained mediocrities could compensate for the loss of a Newton.

Whether America has lost one or more Newtons no on can say for certain. But that many, very many, who should have done creative work of a very high order have, because of defective educational facilities, failed to achieve their destiny, there can be no doubt Because of this America in particular and the world in general are so much the poorer.

A generation ago, American university conditions were something appalling In my own department, students were everywhere misled The only way in which one could get an adequate grounding in the calculus was by going to Europe This subject, which we have already referred to as the basis for most of the higher mathematical analysis, was practically everywhere mistaught. The result was that the potential mathematicians in America were sterilised. One of them, who after his American training, had the corrective of a European experience and now holds an honourable place among American mathematicians, told me ruefully that he would never recover from his early training I have in mind another and younger man from whom his friends and teachers expected great things. His undergraduate training was of the kind referred to above. On top of it he completed a course in one of the best graduate schools on the continent. He has failed to make good, however. His graduate teachers attribute his failure to the false start given by his undergraduate training. I am inclined to accept this explanation, for I know the man, and I am convinced that he had the material in him to make a research worker. I have had my own experience in this connection. Fifteen years after I had received my grounding in the calculus I discovered, I am ashamed to say, in a German university, the University of Berlin, that it had been taught to me falsely, irremediably, and fundamentally falsely. A dislocation of 15 years in one's scientfic life can hardly fail to leave its impress.

There are other subjects, I am informed, in which instruction in American universities was almost as bad as that in mathematics a generation ago. Conditions, however, have greatly improved in the interval. A student would be tolerably safe now in accepting the guidance in mathematics offered in any of the larger universities The like, will, no doubt, be true of other subjects also There is no longer the same urgency as formerly for a student to go abroad. Too much inbreeding, however, is not to be encouraged. A certain amount of circulation is healthful. A university, too, should avoid isolation. It should be in touch with other universities at home and abroad, and ought to be familiar with what is going on in the outside world.

The change in conditions in American universities, the improvement in instruction which has taken place during the last 25 to 30 years, is due primarily to the initiative and self-sacrifice of hundreds of young men who, from time to time, crossed the Atlantic in pursuit of knowledge. After years of study abroad, these men returned to America with a new outlook and new ideas. They were imbued with the spirit of research, and brought it with them into the universities where they received appointments. In the larger institutions there were developments along graduate and research lines. In universities both large and small, the research spirit reacted on the undergraduate work and vitalised it. Bringing a sleepy

*Reprinted from the *Transactions of the Royal Canadian Institute* February 1921.

old text-book routine institution into touch with research has all the effect of connecting a stagnant pool with running water. There are still some pools that would be the better for a little more flow.

The research workers just referred to organised scientific societies. At the meetings of these societies, papers, containing the results of their researches, were read and discussed. Journals were founded for the publication of these papers. The scientific status of the United States and the universities within its borders rose in the eyes of Europe.

The American universities a generation ago were practically all high schools with the exception of the John Hopkins University. They are now a combination of university and high school, and in certain of them the research side has been considerably emphasised. The John Hopkins was a pioneer in research. It was founded primarily as a research institution. An important feature in its policy was the appointment of big men to its professorships. Big men, however, were not always available. Furthermore, it was staitened financially. It did its best under the circumstances, and that meant much. Brick and mortar held a small place in its programme, and its buildings were less pretentious than those of the larger American universities in general. It established scientific journals, and within a few years of its foundation, its prestige in Europe eclipsed that of all other universities on this side of the Atlantic. Other universities supplied with more ample funds have followed the example of the John Hopkins, and have made research a conspicuous feature of their work. Most universities on this continent might take a lesson from the John Hopkins University in regard to the relative emphasis to be laid on men and buildings.

The improvement in the scientific and academic status of American universities during recent years I have attributed primarily to a number of individuals who studied in Europe and brought back with them to America the inspiration of research. To these are to be added scientific graduates of the John Hopkins University distributed among the educational institutions of the continent who had their share in leavening the academic sentiment and spreading the research idea. Those who now have charge of research work in American universities and those who are engaged in industrial research on this side of the Atlantic are, for the most part, pupils of the pioneers in research of whom we have just been speaking.

The research men on the staffs of American universities have done all that is humanly possible for them to do to give efficient instruction in science and to improve research conditions in their institutions. It is up to the university administrators to do their share. Salaries must be increased especially in the junior grades, and research men must not be overloaded with teaching. I could mention one of the largest universities on the continent whose policy it has been to pay its professors the minimum for which it could get them. A few years ago the head of a department in this university told me that the professors' salaries there ranged from $2,000 to $5,000 a year. The President was housed palatially. I could point you to another famous institution, known by name to everyone in this audience, which has on its list professors who are in receipt of a yearly salary of $2,500 or $3,000. Before the war this institution paid its instructors the princely sum of $900 a year. A few weeks ago I learned that it was now anxious to pay $1,800 for a newly-fledged B.A. as instructor in mathematics where it formerly expected to secure a man of Ph.D. grade for half that sum. This is one of the effects of the war. I could name a well-known university where they paid instructors $1,000 a year before the war. Promotion is none too rapid at this institution. Some years ago, so I was told, the head of one of the departments requested the President to increase the salary of one of his instructors to $1,500. The instructor in question was the strongest research man in his department. The President refused the request on the ground that he was not impressive looking. Fortunately, he did not have to wait long for a call elsewhere. He is now professor in another university, where he receives a salary better proportioned to his attainments. An eminent scientist, who was formerly head of a department in an important State university, told me that his two assistant professors, who happened to be married men, were so poorly paid that they had themselves to do their family washing.

That the university administration in America does not always appreciate the efforts of the research man is illustrated in the case of a certain State university which had several men on its staff who were interested in research. These men had published a number of papers in foreign scientific journals. This came to the ears of the Board of Regents. As it happened the Governor of the State was a member of the Board, and he lost no time in communicating with the offending professors and informing them that they were hired to teach and not to write. This story I have from a former professor of the university in question.

The administration of a university may not usually express itself in the same way as the State Governor just referred to, but its policy is frequently just as effective in discouraging research. The business administration of an American university when it comes to engaging instructors is apt to apply the law of supply and demand ruthlessly. It takes no account of the motives or ideals of those who are seeking positions on the teaching staff. Among the candidates may be one whose dearest desire in life is to find the opportunity to do research. This privilege he would not forego for anything which fortune or favour could offer him. He has already made his first contributions to knowledge, and there is every reason to believe that Nature has endowed him with gifts of the highest order. The findings of research appear to him to be the most permanent contribution to our civilisation. The great pathfinders in science he regards as the highest product of the race. By identifying himself with science through research it seems to him that he associates himself more closely with the eternal than he can do in any other way. The only opportunity to do research would appear to lie in a university career. The administration offers him a beggarly pittance barely sufficient to hold soul and body together. This he accepts in the expectation that he will find the time for research. Vain delusion!

He is loaded down with lectures and tutorial work on the general business principle that the more hours his employers squeeze out of him, the more they are getting for their money. This is the kind of policy which kills the goose that lays the golden egg. The years pass. Possibly our research man gets married. He has no margin to come and go on. Promotion comes slowly. Financial worries multiply. He finds himself at last compelled to abandon his long-cherished plans for research. He broods over the futility of his sacrifices, and eats his very heart out.

Some there are who are more fortunate, who find it possible to reserve a little time for research and who manage to produce, though under handicap. A few, too, there are who, after years of struggle, arrive in a position where they are masters of the major part of their time, and can devote themselves to research, if in the intervening years their productive ardour has not abated.

If, then, scientific productivity in the American univesities to-day is greater than it was a quarter-of-a-century ago, the credit therefore is due not to the university administrations, but, as we have already stated, to members of the academic staffs, which members are also responsible for the increased efficiency of scientific instruction in the universities. For the more advanced instruction these men often receive no remuneration. They are permitted as a privilege to undertake this work in addition to their regular work. There is no eight-hour day for the research worker. For overtime he does not receive time-and-a-half pay He gives the extra time gratis. The layman may think that the scientist is paid for the articles he publishes in the technical journals. This, howe-ever, is not the case. He does this work gratis also. The editorial work on the scientific journals is, in general, done without remuneration I may add, furthermore, that there is no money in the publication of a scientific treatise or a more advanced text-book

The man on the street will say anyone who does so much work gratis is not practical. There is this side of it, however, that when a man has toiled a lifetime to make a fortune, the very best that he can do with it is to endow research. His benefaction to the race is then of the same effect as that of the research worker The man of wealth contributes indirectly to the welfare of mankind. He first acquires his wealth and then uses it to subsidise the research worker. The latter makes his contribution directly. Why should we say he is less practical than the business man who has accumulated wealth? It may be that, under stress of circumstances, he consents to accept less than a decent living salary. The business administration of the university which is willing to take advantage of his position, however, can hardly be called practical for its policy is, in the long run, detrimental to the university, to science, and to the best interests of the nation.

In European universities the position of research is less incidental than in the general run of American Universities. In Germany the university is essentially a research institution, and every member of the teaching staff, as we have already indicated, is appointed on a basis of research qualifications. Practically the same result is secured in France in another way. The professoriate there is recruited from the most select of the select material which is admitted to the schools for genius, to which I have already made reference. In certain of the English universities the professorial standard is safeguarded by a system of so-called electors. For those who are not familiar with the system I may say that when a chair becomes vacant, a number of men are named whose duty it is to select a man to fill the place. These are known as electors. They are usually men of technical knowledge Certain of them are from the institution concerned The others are outsiders. The principal evil the system is intended to guard against is appointment by local pull. The voice of the outsiders, I am told, is usually the determining factor in making the selection. I have in mind a case where there were five electors, of whom three were from outside the institution The two local electors felt under obligation to support a colleague who was a candidate for the position. The outside electors, however, said that they must have a stronger research man, and it was decided in this sense.

(To be continued).

## NOTICES OF BOOKS.

*A Text Book of Inorganic Chemistry for University Students.* By J. R. Partington, D.Sc., M.B.E. Pp. xiii + 1062. 1921. London. Macmillan & Co., Ltd. Price 25s. net.

This text-book is primarily intended for students who have completed an introductory course of matriculation standard, although the more elementary parts of the subject are included so as to make the book complete in itself. It is not written for any particular examination, but should meet the requirements in inorganic chemistry of students preparing for the examinations of the Intermediate and Pass B Sc. of British universities. Brief accounts of technical processes and the elements of physical chemistry are included, with worked examples on the latter Amongst the section on Physical Chemistry, the Atomic Theory and the Periodic Law are given special prominence.

Summaries of chapters have been added where this addition has seemed likely to be useful in affording assistance in revision, and examples on all chapters are provided, the answers being collected together at the back of the book.

The book is interspersed with 439 illustrations, thus greatly hepling the student to form mental pictures of the subject being discussed.

*Chemical Technology and Analysis of Oils, Fats, and Waxes.* Vol. I. Sixth Edition. By Dr. J. Lewkowitsch, M.A., F.I.C. Edited by by George H. Warburton. Pp. xviii. + 682. 1921. London. Messrs. Macmillan & Co., Ltd. Price 36s. net.

This work is published in three volumes. The first is divided into twelve chapters; Chapter I, entitled "The Classification of Oils, Fats, and Waxes—Physical and Chemical Properties of Oils, Fats, and Waxes," deals with the chemical constitution of fats and the preparation and properties of pure glycerides. Chapter II., on the "Saponification of Fats and Waxes," gives an account of the different methods of saponification employed. The "Chemical and Physical Properties of the Constituents of Fats and Waxes" are discussed in the next chapter

Methods for the examination of oils, fats, and waxes, both physical and chemical, qualitative and quantitative, are next given, this part running into nine chapters.

No index is given at the end of this volume; this is reserved for the end of Vol. III., which will contain a complete index for the whole work

*A Dictionary of Applied Chemistry.* Vol. I. (A-Calcium). By SIR EDWARD THORPE, C.B., LL.D., F.R.S. 1921. Pp. x.+752. London: Longmans, Green & Co. Price 60s. net.

The previous edition has been thoroughly revised, and many new articles have been added, for instance, on the Natural Organic Colouring Matters, and on the Relation of Colour to Chemical Constitution.

Extensive additions have been made to subjects of technical importance, such as sulphuric acid, nitric acid, chlorine, the metallurgy of the commercially important metals, oils, fats, &c.

A list of the contributors, with the titles of their articles, is prefixed to the several volumes, also a list of the abbreviations used in the Dictionary of the titles of Journals and Books which have been used as an authority for a statement appearing, has been inserted.

*Treatise on General and Industrial Inorganic Chemistry.* By Dr. ETTORE MOLINARI. Second Edition. Translated by THOMAS H. POPE, B.Sc., F.I.C., A.C.G.I. Pp. xix.+876. 1920. London: J. & A. Churchill. Price 42s. net.

This second edition is a translation of the fourth Italian edition. The translation of the original text has been adhered to as faithfully as possible, prices of chemicals, &c., have been converted into English currency per kilogrm. in the case of fine chemicals, and per ton in other instances.

The author is Professor of Chemistry at the Milan Polytechnic, and this book arose out of the author's attempts to devise a general course of inorganic chemistry for the students of this college, which would enable them to grapple with the problems of industrial chemistry in a better way than had been possible formerly

For instance, wherever possible, the author has replaced laboratory sketches for sketches of industrial apparatus collected by him from the best works on chemical technology, from patents, or directly from practice in works which he has visited.

The first sections of the work are devoted to a short historical sketch of the progress of chemistry from the earliest times, and to a general discussion of physical laws. Part II. deals with the non-metals and their compounds, also with some of the rarer metals which act like non-metals in some of their reactions.

The third portion, which deals with the metals and their compounds, is preceded by a section on the fundamental laws of electrochemistry, and by an amplification of the electrolytic theory of solutions.

The book closes with a short summary of the periodic system of the elements.

To indicate the importance of each substance as it is dealt with in its position in the book, the author has summarised its present and past importance by means of statistics, including its commercial price; in this way one can obtain a good idea of the uses to which the substance under discussion is put to.

The book contains 328 illustrations, together with two phototype plates, and also a good index which runs into 17 pages.

*Vitamines, Essential Food Factors.* By BENJAMIN HARROW, Ph.D London: George Routledge & Sons

In this interesting book the subject of vitamines, one of the latest advances in the science of nutrition, is treated in a popular manner. It is astonishing to learn that a subject of such vast importance has only been recognized within the last ten years The "vitamines," that subtle something in food-stuff whose presence or absence means life or death, is so very little understood that the very terms used in connection with it are unfamiliar to the vast majority of living people. The object of the author is to make known in a more general sense, the laborious researches that have been carried on during the last few years on this important subject.

The first part of the book is devoted to a survey of the principles of nutrition *prior* to the time when vitamines were recognised; the knowledge involved in such subjects as calories, carbohydrates, amino-acids, soap, and glycerine, is discussed in a way and in language that presents no difficulty to the layman. Six chapters are devoted to the subject of vitamines proper, their effect upon plant growth, disease, and life, are fully discussed, and the concluding chapter treats with "Practical Applications," which is certainly the most important section of the book, and is one that should be studied by everyone.

The perusal of the book, which in itself is of very great interest, brings to the reader the conviction that the further unfolding and diffusion of this important science will help greatly in the struggle that has engaged the human race from its origin in the distant past with ever-increasing intensity up to the present day—the grim fight between life and death, health and disease, happiness and misery. The author in his endeavour to bring vitamines to the attention of the general reader has done well.

A very complete bibliography is included which will be of great value to those who wish to pursue the subject further, and a complete index makes reference easy.

*The Paper-Makers' Directory for All Nations.* 1921. London. Dean & Son, Ltd. Price 21s.

In the editorial preface, the disastrous effect of the recent addition to the postage rates is referred to, and the serious influence upon the present trade depression is pointed out It is also announced that it is now possible to revise and publish the Austrian and German Mill sections, which is done very completely; one cannot help noticing that the announcements of manufacturers in England and Wales occupy 57 pages, while those of Germany and Austria fill 94. The book consists of three main sections, arranged alphabetically, and records full details regarding the paper, pulp, and board mills of the world. The first part deals with mills in the United Kingdom (with many useful lists of allied trades); the second with those in the Colonies and abroad; and the third gives a comprehensive register of mill pro-

ductions under some 400 trade designations, classified according to class of goods manufactured, country of origin, and name of firm. Attention is drawn to the index of names of advertisers that is given at the end of the book with its obvious advantages

The Directory is very well got up, and does credit to its publishers; it is, of course, a necessity to all purchasers of paper in quantity.

## CORRESPONDENCE.

[In our issue of May 27, we published a letter from Sir Robert Robertson, who drew attention to a statement that was made by Prof. Wilsmore in his Address.* We have just received the following explanation from Prof. Wilsmore.—EDITOR.]

### CHEMISTS AT £2 0s. 6d. PER WEEK.

*To the Editor of the Chemical News.*

SIR,—Sir Robert Robertson has called my attention to a regrettable error in my Presidential Address to the Chemical Section of the Australasian Association for the Advancement of Science (CHEMICAL NEWS, May 6, 1921, cxxii., 209), whereby it is made to appear that the chemists who were advertised for early in 1915 at £2 0s. 6d. per week were required for work in the Research Department at Woolwich. In reality it was the Inspection Department at the Royal Arsenal, Woolwich, which was responsible for the advertisement offering this "wage" to fully-trained chemists. The advertisement in question is quoted in full in a letter from Sir William Tilden to the CHEMICAL NEWS of February 25, 1915, cxi., 108, from which it will be seen that, with the exception of the above-mentioned error, my paraphrase was substantially correct. In any case, however, it was far from my intention to impute responsibility for this advertisement to any member of the scientific staff of the Research Department at Woolwich, least of all to Sir Robert Robertson, who has done probably more than any other man to raise the status of chemists in British Government Departments; and I regret that my words should have conveyed a contrary impression. In this connection I wish to lay stress on the value of the work which was carried out during the war in the Research Department at Woolwich by Sir Robert Robertson and his staff. Although some of that work has since been released for publication, only those who were behind the scenes can appreciate fully its importance to the nation in the critical times through which we have passed. In fact, much of the success of the late Department of Explosives Supply was undoubtedly due to the guidance and advice which at all times were placed ungrudgingly at its disposal by Sir Robert Robertson and his former colleagues in the Research Department.—I am, &c.,

N. J. M. WILSMORE.

University of Western Australia,
Perth, June 20.

*The present position of Chemistry and Chemists by Prof. N. W Wilsmore, CHEMICAL NEWS, May 6, 1921.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences.* Vol. clxxiii., No. 1.

"Interaction of Oxalic Acid and Iodic Acid: Second part—The Influence of Different Catalysts"—By M. Georges Lemoine.

"Action of Heat on Allyl Alcohol in the Presence of Different Catalysts."—By MM. Paul Sabatier and Bonasku Kubota.

"Ammonium Molybdate."—By M. Georges Tauret.

"The Spectra of Silicon from Molten Salts and Steels appearing with Quantitative Sensitiveness." —By M. A. De Gramont.

"Superficial Tension of Monomolecular Layers." —By M. A. Marcelin.

Vol. clxxiii., No. 2.

"Contribution to the Study of the Stability of Nitrocellulose Powders."—By M. Fric.

"Synthesis of Tertiaryalcohols from Methylethyketone."—By MM. Pariselle and Simon.

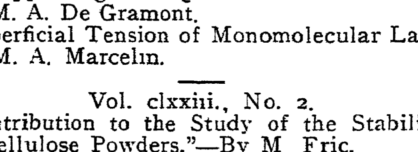
"Hydrogenation of Some Oils of Marine Animals."—By M. H. Marcelet.

"Rotatory power of Crystalline Masses."—By M Louis Longchambou.

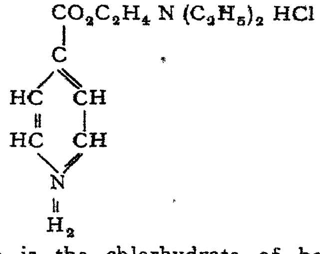
*Journal de Pharmacie de Belgique,* No. 27. July 3, 1921.

"Methods of Distinguishing between Cocaine Chlorhydrate, Novocaine, and Stovaine, and their Examination in Binary Mixtures."—By MM. G. Batta and C. Jenot. Owing to the fairly frequent adulteration of samples of cocaine, the above-named pharmacists of the University of Liége have given in this Journal a number of distinguishing tests.

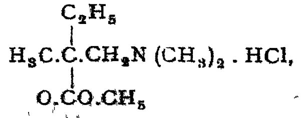
Chlorhydrate of cocaine has the following constitution :—



Novocaine is the chlorhydrate of $p$-aminobenzoyl diaminoethane.



Stovaine is the chlorhydrate of benzoylethyldi methylaminopropanol.



They have set down in a table the properties and reactions to certain chemicals of these three anæsthetics; we have reproduced it here.

| Formula | Chlorhydrate of Novocaine $C_{13}H_{20}N_2O_2HCl$ | Chlorhydrate of Cocaine $C_{17}H_{21}NO_4HCl$ | Stovaine $C_{14}H_{21}NO_2HCl$ |
|---|---|---|---|
| Molecular weight | 272·5 | 339·5 | 271·5 |
| Content of hydrochloric acid | 13·4 | 10·8 | 13·4 |
| Content of nitrogen | 10·2 | 4·1 | 5·2 |
| Physical properties | Colourless needles; inodourous; feebly bitter taste | Anhydrous crystals; colourless, odourless; bitter taste | Crystalline powder; white, odourless; bitter taste |
| Solubility in water | Soluble in 1 part water | Soluble in 0·75 parts of water | Soluble in two parts of water |
| Solubility in alcohol | Soluble in 30 parts of alcohol | Soluble in 60° alcohol; difficultly soluble in absolute | Soluble; less so in absolute |
| Solubility in chloroform | Slightly soluble | Soluble | Soluble |
| Solubility in ether | Insoluble | Insoluble | Insoluble |
| Solubility in carbon bisulphide | Insoluble | Practically insoluble | Hardly soluble |
| Solubility in benzol | Insoluble | Insoluble | Hardly soluble |
| Melting point | +156° | 183° | 175° |
| Polarised light | No action | | No action |
| Reaction to litmus | Neutral | Neutral | Acid |
| Action with $KNO_2$+β-naphthol | Scarlet red precipitate | No action | No action |
| Action with resorcinol | Intense red | No action | No action |
| Action with phenol | Orange red | No action | No action |
| Action with potassium permanganate | Rapid decolouration | Very slow decolouration | Slow decolouration |
| Action with dilute $H_2SO_4$ | No odour of ether; no crystals | Odour of methylbenzoic ether; crystals of benzoic acid | Odour of benzoic ether; crystals of benzoic acid |
| Action with ammonia | Very feeble precipitate appearing after some minutes; liq. opalescent | Well formed crystals; clear liquid | Liquid becomes immediately milky |
| Action with caustic potash | Oily precipitate becoming crystalline | White precipitate | White oily precipitate |
| Action with borax | No precipitate | White precipitate | White precipitate, less soluble than the cocaine |
| Action with sodium phosphate | No precipitate | Thin opalescence in concentrated solutions | White milky precipitate |
| Action with ferricyanide | Blue precipitate | No precipitate | Precipitate after long standing |
| Action with $HNO_3$+KOH | No odour of benzoic ether | Odour of benzoic ether | Odour of benzoic ether |
| Action with potassium chromate | No precipitate | Precipitate only when HCl is added | Oily precipitate, before the addition of HCl |
| Action with gold chloride | Brown precipitate | Clear yellow precipitate | Clear yellow precipitate |
| Action with $HgI_2$+KI | Yellowish-white precipitate | Yellowish-white precipitate, collecting easily | Yellowish-white precipitate |
| Action with KI×I | Precipitate soluble in HCl | Precipitate collecting in concentrated solutions | Precipitate |
| Action with Cl and $PdCl_2$ | Solution blackens with chlorine alone; no red precipitate | Red precipitate when the solution is not too dilute | Thin red colouration |
| Lime water | The addition of small quantities of the reagent gives a white precipitate (2 per cent solution) | Two or three drops give a precipitate (2 per cent solution) | Two or three drops give a precipitate (2 per cent solution) |
| Fuming nitric acid | Combination of the mixture; residue of very spongy carbon | The mixture does not ignite | The mixture does not ignite. |

In conclusion, the authors state that the anæsthetics can easily be identified one from the other in pure aqueous solutions by means of the reactions given above, especially the reactions given with resorcinol and nitric acid, which will easily distinguish between novocaine and the chlorhydrate of cocaine and stovaine, and the sodium phosphate reaction which will distinguish between stovaine and the others. The reaction of novocaine with resorcinol should prove useful for toxicological researches, as it is sensitive with 0·0001 grm. of this anæsthetic

The authors have been able to reveal the presence of less than 0·5 per cent of novocaine in chlorhydrate of cocaine or in stovaine by either the $\beta$-naphthol or the resorcinol tests.

Sodium phosphate will reveal the presence of less than 10 per cent of stovaine in novocaine or in chlorhydrate of cocaine, the borax or the sulphuric acid reaction detecting less than 10 per cent of cocaine in novocaine.

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*Transactions of the American Electro-Chemical Society.* Vol. xxxvii., 1920.

"Arc Images in Chemical Analysis." By Wm. Roy Mott. In this interesting paper the author describes a new method, rapid, delicate, semi-quantitative, and comprehensive, for the identification of the elements in simple and complex mixtures. Characteristic tests are given for 65 different elements, and it is claimed that any of these can be identified in their ores in a few minutes.

The method makes use of, and combines in one operation certain points in spectrum analysis, fire assay, micro-chemistry, and fractional distillation, and depends upon the phenomena which occur when a sample of the material to be tested is introduced into an arc struck between carbon poles.

The paper is devoted more to the results obtained than to the actual working details of the experiment, but it appears that when a sample of about 0·5 grm. of the material is placed in a depression in the positive carbon and the arc is started, various phenomena are observed, such as changes in the shape and colour of the arc itself or of the flame tip, and the emission of sparks, smoke, or odour, which are characteristic of various elements. The order of distillation of the elements, and the height at which they condense upon the upper carbon, are made use of; special attention being paid to the nature and colour of the deposits left upon the electrodes and the extent to which they are modified by the addition of simple reagents, as in ordinary blowpipe analysis.

The apparatus consists simply of a direct-current arc lamp, enclosed in a hood fitted with a pinhole diaphragm, and a lens so arranged that an enlarged image of the arc is thrown upon a screen in a dark room.

The method can be applied directly to all ores, minerals, refractories, oxides, oxy-compounds, carbides, metals, and alloys. The delicacy of the test varies, but it is claimed that, in the cases of the uncommon, refractory, and valuable elements, which by the usual wet methods present the most difficulty, amounts in the order of 0·02 per cent can be detected with ease. In all cases a good idea can be obtained of the relative quantities present.

There is no doubt that, could the method be brought into general use, it would form a valuable supplement to present methods.

We congratulate the author upon his work, of which we should be interested to see a more detailed account than can be given in a single paper.

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## NOTES.

INSTITUTE OF METALS.—The following papers are expected to be submitted at the Annual Autumn Meeting of the Institute of Metals, to be held in Birmingham on September 21-23:—

"The Properties of Some Nickel-Aluminium-Copper Alloys." By Prof. A. A. Read, D.Met. (Cardiff), and R. H. Greaves, M.Sc. (Woolwich).

"The Effect of Increasing Proportions of Lead upon the Properties of Admiralty Gun-Metal." By R. T Rolfe, F.I.C. (Bedford).

"The Casting of Brass Ingots." By R Genders, M.B.E., B.Met. (Woolwich).

"The Density of the Zinc-Copper Alloys." By T. G. Bamford, M Sc. (Birmingham).

"Experiments in the Working and Annealing of Copper." By F. Johnson, D.Sc. (Birmingham).

"The Effects of Progressive Cold-Drawing upon some of the Physical Properties of Low-Tin Bronze." By W. E. Alkins, M Sc. (Manchester) and W. Cartwright (Buxton)

"The Extrusion Defect." By R. Genders, M.B.E., B.Met. (Woolwich).

"The Use of the Scleroscope on Light Specimens of Metals." By F. S. Tritton (Teddington).

"The Annealing of Rolled Zinc" By D. H. Ingall, B.Sc. (Birmingham). ...

"The Constitution and Age-Hardening of the Alloys of Aluminium with Magnesium and Silicon." By D. Hanson, D.Sc. (Teddington) and Miss M. L. V. Gayler, M.Sc. (Teddinton).

"Electrolytic Etching of Metals." By F. Adcock, M.B.E., B.Sc. (Sheffield).

"Electron—the High Magnesium Alloy." By S. Beckinsale, B.Sc. (London).

Papers will be presented and discussed at the morning sessions, the afternoons being devoted to visits to works, and the evenings to social events, including a reception by the Lord Mayor, and a garden party, whilst to conclude the meeting there will be a motor trip to Kenilworth, Warwick, and Stratford-on-Avon. A ballot for the election of members is now being arranged for the convenience of those persons who desire to participate in the Birmingham meeting. Full particulars can be obtained from the Secretary, Mr. G. Shaw Scott, M.Sc., 36, Victoria Street, London, S.W.1. Since the holding of the inaugural Autumn Meeting of the Institute in Birmingham in 1908, the membership has grown from 200 to over 1300. The coming meeting, marking as it does the first visit of the Institute to its old home, will afford a striking indication of the wonderful strides that have been made by the Institute of Metals since its timely foundation thirteen years ago.

BOARD OF TRADE ANNOUNCEMENT.—In accordance with the provisions of Section 2 (6) of the Dyestuffs (Import Regulation) Act, 1920, the President of the Board of Trade has appointed the following: Mr. W. J. U. Woolcock, C.B.E., M.P. (Chairman), Mr. Percy Ashley, C.B (Board of Trade), Sir Henry Birchenough, Bart., K.C.M.G., Mr. W. H. Dawson, Mr. George Douglas, Mr. E. V. Evans, O.B.E., F.I.C., Dr. M. O. Forster, F.R.S. (Director of the Salter Institute of Industrial Chemistry), Mr. L. B. Holliday, Dr. Herbert Levinstein, F.I.C., Prof. G. T. Morgan, F.R.S., Mr. James Morton, Mr. Max Muspratt, Mr. Thomas Taylor, Mr Norman Thomas (Admiralty), Mr. G. S. Witham (War Office), together with another representative of dye-using interests to be appointed shortly, to be a Committee to advise the Board of Trade with respect to the efficient and economical development of the dye-making industry.

## New Patents.

THIS List is specially compiled for the *Chemical News* by Messrs Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W.C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

18333—Air Reduction Co., Inc.—Method of producing hydrocyanic acid and cyanides. July 6.

18334—Air Reduction Co., Inc.—Method of producing hydrocyanic acid. July 6

18092—Bitumul-Matita Soc. Anon Romana—Manufacture and treatment of bitumen. July 4.

18553—Claessen, C—Process for manufacture of elastic flexible masses from nitro cellulose. July 8.

18479—Lorival Manufacturing Co, Ltd.—Manufacture of condensation of phenolic bodies with aldehydic compounds. July 7.

*Specifications published this Week.*

142448—Ges. Fur Chemische Industrie in Basel.—Manufacture of substantive ortho-oxy-ayodyestuffs and their application in dyeing.

165639—Carpmael, W.—Furnaces for the manufacture of hydrochloric acid and sodium sulphate.

*Abstract Published this Week.*

*Bitumen and Mineral Oil.*—Mr. M. E. Fyleman of 103, Cannon Street, London, has obtained a Patent No 163519 for an improved separation of bitumen or mineral oil from rock or sand impregnated therewith. The sand, etc., is treated with an aqueous solution of substances promoting the formation of froth such as alkali soaps, turkey red oil, saponin or glue, alkali salts or hydromides or dilute acids, so that the bitumen or oil separates and rises to the surface or sinks to the bottom or forms an emulsion The oil, etc., is then separated by a washing process. Heat may be applied to render the oil or bitumen fluid or a solvent such as paraffin oil added.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.



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THE CHEMICAL NEWS.

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## INTERNATIONAL PHYSICO-CHEMICAL SYMBOLS.*

(AUTHORISED FOR PUBLICATION BY THE COUNCIL OF THE CHEMICAL SOCIETY).

AT the meeting of the Council of the International Association of Chemical Societies, held in Brussels in September, 1913, it was decided that the International Commission for the Unification of Physico-Chemical Symbols "Shall appoint a small Working Committee of five members, not necessarily members of the Council, to receive and consider the reports of the National Committees, and further to suggest methods for the organisation and carrying out of future work." In accordance with this decision, the President of the International Commission (the late Sir William Ramsay) nominated the following gentlemen to serve on the Working Committee, namely, Sir William Ramsay (Chairman), Dr. Friedrich Auerbach, Prof. P. A. Guye, Prof. P. J. Walden, and Prof. Alex Findlay (Secretary), and these nominations were approved by the Commission.

In accordance with the decision of the International Commission, approved by the Council (Report, 1913, p. 27), the list of symbols recommended by the Commission was sent to the different societies affiliated with the International Association of Chemical Societies, as well as to the Ausschuss für Einheiten und Formelgrössen and the International Electrotechnical Commission, and the request was made that these societies or bodies should intimate to the Secretary any criticisms or suggestions which they might have to make regarding the symbols recommended.

The criticisms and suggestions received were considered at a meeting of the Working Committee held in Paris on May 29 and 30, 1914. At this meeting, Dr. Charles Marie was also present by invitation of the Chairman.

At the outset, the following general principles were adopted:

1. The decisions of the Committee shall be restricted to symbols for quantities of chemical or physico-chemical importance.

2. In respect of symbols for quantities used, more especially in mathematics, physics, and the various branches of applied mathematics and physics, the Committee shall restrict itself to *noting* the symbols which have been recommended or adopted by the scientific bodies specially interested in these quantities. With regard to the latter, it was resolved to include in the list of symbols only those about which there is general agreement among the specially competent bodies.

3. The decisions of the Committee shall be restricted to symbols for quantities, and shall not extend to signs for the names of units.

4. The Committee considers it to be inadvisable that any attempt should be made to *compel* authors to use the symbols which the Committee recommends. Every means, however, should be taken to *encourage* the use of these symbols, which would be revised at such times and in such ways as might appear to the Commission to be advisable.

5. With regard to the symbols for quantities which are employed in different branches of pure or applied science, the Committee considers that it is not possible in every case to obtain agreement between the different sciences. It is of opinion, therefore, that the symbols suggested should be such as might find general acceptance by chemists and physico-chemists.

6. The Committee recommends that in every case authors should express their results in C.G.S. units.

On the basis of these general principles, the Committee drew up, for the approval of the International Commission, the list of symbols given below. This list of symbols was circulated among the members of the Working Committee, and was returned to me approved and initialled by Sir William Ramsay, Dr. Auerbach, Professors Guye and Walden, and Dr. Marie It was the intention, after taking account of any remarks made by the members of the Committee, to circulate the final list for signature by the members of the Committee, but the outbreak of war prevented this from being done. These remarks have, however, been taken account of in the list given below, which may be taken as being practically identical with that initialled by the individual members of the Committee.

In accordance with a recommendation of the Working Committee, it has been thought well to append to the list of symbols the reasons for the choice of symbol made by the Committee in certain debated cases.

ALEX. FINDLAY,

*Secretary to the Working Committee.*

*List of Symbols recommended by the Working Committee of the International Commission for the Unification of Physico-Chemical Symbols* (1914).

### 1. *Mathematical Symbols.*

| | Usual symbol. | Alternative symbol. |
|---|---|---|
| Base of natural (Napierian) logarithms ... ... | $e$ | |
| Diameter ... ... ... | $d$ | |
| Radius ... ... ... | $r$ | |
| Ratio of circumference to diameter ... ... | $\pi$ | |
| Summation ... ... | $\Sigma$ | |
| Variation ... ... | $\delta$ | |
| Total differential ... ... | $d$ | |
| Partial differential ... | $\partial$ | |

### 2. *Universal Constants.*

| | Usual symbol. | Alternative symbol. |
|---|---|---|
| Acceleration due to gravity | $g$ | |
| Mechanical equivalent of heat | $J$ | |
| Avogadro's constant [number of molecules in 1 gram-molecule (mole)] ... | $N$ | |
| Gas constant per mole ... | $R$ | |
| Faraday's constant (number of coulombs per gram-equivalent of an ion) ... | $F$ | |
| Charge on an electron ... | $e$ | |

* Reprinted from the *Journal of the Chemical Society*, April, 1921.

### 3. *General Physics and Chemistry.*

| | | |
|---|---|---|
| Length ... ... ... | $l$ | |
| Height ... ... ... | $h$ | |
| Mass ... ... ... | $m$ | |
| Time ... ... ... | $t$ | |
| Volume ... ... ... | $v, V$ | |
| Density (mass per unit volume) ... ... | $d$ | $D$ |
| Pressure ... ... ... | $p, P$ | |
| Concentration ... ... | $c, C$ | |
| Mole fraction ... ... | $x$ | |
| Critical constants: pressure, volume, temperature (centigrade), temperature (absolute), density ... | $p_c, v_c$ <br> $t_c, T_c$ <br> $d_c$ | |
| Reduced quantities: pressure volume, temperature density ... ... | $p_r, v_r$ <br> $t_r, T_r$ <br> $d_r$ | |
| van der Waals's constants ... | $a, b$ | |
| Fluidity ... ... ... | $\phi$ | |
| Viscosity ... ... | $\eta$ | |
| Surface tension ... ... | $\gamma$ | $\sigma$ |
| Diffusion coefficient ... | $\Delta$ | |
| Atomic weight ... ... | $A$ | |
| Molecular weight ... ... | $M$ | |
| Velocity coefficient of reaction | $k$ | |
| Equilibrium constant ... | $K, (K_c, K_p)$ | |
| van't Hoff coefficient ... | $i$ | |
| Degree of dissociation (electrolytic, thermal, etc.) | $a$ | |

### 4. *Heat and Thermodynamics.*

| | | |
|---|---|---|
| Temperature (centigrade) ... | $t$ | $\theta$ |
| Temperature (absolute) ... | $T$ | |
| Critical temperature ... | $t_c, T_c$ | |
| Reduced temperature ... | $t_r, T_r$ | |
| Critical solution temperature | $t_{cs}, T_{cs}$ | |
| Quantity of heat ... ... | $Q$ | |
| Entropy ... ... ... | $S$ | |
| Specific heat ... ... | $c$ | |
| Specific heat at constant pressure ... ... | $c_p$ | |
| Specific heat at constant volume ... ... | $c_v$ | |
| Ratio of specific heats, $c_p : c_v$ | $\gamma$ | |
| Molecular heat ... ... | $C$ | |
| Molecular heat at constant pressure ... ... | $C_p$ | |
| Molecular heat at constant volume ... ... | $C_v$ | |
| Latent heat per gram ... | $l$ | |
| Latent heat per mole ... | $L$ | |
| Maximum work (diminution of free energy) ... | $A$ | |

### 5. *Optics.*

| | Usual symbol. | Alternative symbol. |
|---|---|---|
| Wave-length of light ... | $\lambda$ | |
| Refractive index ... ... | $n$ | $n_r$ |
| Specific refractive power (Gladstone and Dale) ... | $r_G, [r_G]^{t^\circ}_{\lambda}$ | |
| Specific refractive power (Lorentz and Lorenz) ... | $r_L, [r_L]^{t}_{\lambda}$ | |
| Molecular refractive power | $R_G, R_L$ <br> $[R_G]^{t^\circ}_{\lambda}, [R_L]^{t^c}$ | |
| Angle of optical rotation ... | $a$ | |
| Specific rotatory power ... | $[a]$ | |
| Molecular rotatory power ... | $M[a]$ | |
| Specific magnetic rotation ... | $[\omega]$ | |
| Molecular magnetic rotation | $M[\omega]$ | |

### 6. *Electricity and Magnetism.*

| | | |
|---|---|---|
| Quantity of electricity ... | $Q$ | |
| Current intensity ... ... | $I$ | |
| Resistance ... ... | $R$ | $W$ |
| Electromotive force ... | $E$ | |
| Electrode potential, or discharge potential of an ion ... ... ... | $E$ | $\epsilon$ |
| Electrode potential referred to the normal hydrogen or normal calomel electrode respectively, the potential of which is taken as zero ... ... | $E_h, E_c$ | $\epsilon_h, \epsilon$ |
| Normal potential, *i.e.*, the electrode potential referred to the normal hydrogen or normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration ... | $_0E_h, {}_0E_c$ | $_0\epsilon_h, {}_0\epsilon_c$ |
| Dielectric constant ... | $\epsilon$ | |
| Conductivity (specific conductance) ... ... | $\kappa$ | |
| Equivalent conductivity ... | $\Lambda$ | |
| Equivalent conductivity at different dilutions—volumes in litres containing 1 gram-equivalent ... | $\Lambda_{10}, \Lambda_v, \Lambda_\infty$ | |
| Equivalent conductivity of kation and of anion ... | $\Lambda_k, \Lambda_a$ | |
| Equivalent conductivity of specified ions... ... | $\Lambda_{K^\cdot}\ \Lambda_{Cl'}$ | |
| Molecular conductivity ... | $\mu$ | |
| Velocity of kation and of anion in cm./sec. when the potential gradient is 1 volt per cm. ... | $U_k, U_a$ | |
| Transport number of kation and of anion ... ... | $n_k, n_a$ | |
| Magnetic permeability ... | $\mu$ | |
| Magnetic susceptibility ... | $\kappa$ | |

### *List of Symbols, arranged Alphabetically.*

| Symbol. | Name of quantity. |
|---|---|
| $A$ | Atomic weight; maximum work |
| $a$ | Van der Waals's constant |
| $b$ | Van der Waals's constant |
| $C$ | Concentration; molecular heat |
| $c$ | Concentration; specific heat |
| $C_p, C_v$ | Molecular heat at constant pressure, and at constant volume |
| $c_p, c_v$ | Specific heat at constant pressure, and at constant volume |
| $D$ | Alternative symbol for density |
| $d$ | Diameter; total differential; density |
| $d_c$ | Critical density |
| $d_r$ | Reduced density |
| $E$ | Electromotive force; electrode potential |
| $e$ | Base of Napierian logarithms; charge on an electron |
| $E_h, E_c$ | Electrode potential referred to the normal hydrogen or the normal calomel electrode, respectively, the potential of which is taken as zero |
| $_0E_h, {}_0E_c$ | Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration |

| | |
|---|---|
| $F$ | Faraday's constant (number of coulombs per gram-equivalent of an ion) |
| $g$ | Acceleration due to gravity |
| $h$ | Height |
| $I$ | Current |
| $i$ | Van't Hoff's coefficient |

| Symbol. | Name of quantity. |
|---|---|
| $J$ | Mechanical equivalent of heat |
| $K$ | Equilibrium constant |
| $K_c, K_p$ | Equilibrium constant, when molar concentrations and partial pressures respectively are employed |
| $k$ | Velocity coefficient of reaction |
| $L$ | Latent heat per mole |
| $l$ | Length; latent heat per gram |
| $M$ | Molecular weight |
| $M[\alpha]$ | Molecular rotatory power |
| $M[\omega]$ | Molecular magnetic rotatory power |
| $m$ | Mass |
| $N$ | Avogadro's constant (Loschmidt's number) or number of molecules in 1 gram-molecule |
| $n$ | Refractive index |
| $n_k, n_a$ | Transport number of kation and of anion |
| $n_r$ | Refractive index (alternative symbol) |
| $P$ | Pressure |
| $p_c, p_r$ | Critical pressure: reduced pressure |
| $Q$ | Quantity of heat; quantity of electricity |
| $R$ | Gas constant per mole; electrical resistance |
| $R_G, R_L$ | Molecular refractive power, according to Gladstone and Dale, and to Lorentz and Lorenz respectively |
| $r$ | Radius |
| $r_G, r_L$ | Specific refractive power according to Gladstone and Dale, and to Lorentz and Lorenz respectively |
| $S$ | Entropy |
| $T$ | Absolute temperature |
| $T_c$ | Critical temperature (on the absolute scale) |
| $T_r$ | Reduced temperature (absolute) |
| $T_{cs}$ | Critical solution temperature (absolute) |
| $t$ | Time; temperature (centigrade) |
| $t$ | Critical temperature (centigrade) |
| $t_{cs}$ | Critical solution temperature (centigrade) |
| $t_r$ | Reduced temperature (centigrade) |
| $U_k, U_a$ | Velocity of kation and of anion in cm./sec. when the potential gradient is 1 volt per cm. |
| $V$ | Volume |
| $v$ | Volume |
| $v_c, v_r$ | Critical volume: reduced volume |
| $W$ | Electrical resistance (alternative symbol) |
| $x$ | Mole fraction |
| $\alpha$ | Degree of dissociation (electrolytic, thermal, etc.); angle of optical rotation |
| $[\alpha]$ | Specific rotatory power |
| $\gamma$ | Surface tension; ratio of specific heats |
| $\Delta$ | Diffusion coefficient |
| $\delta$ | Variable |
| $\partial$ | Partial differential |
| $\epsilon$ | Electrode potential (alternative symbol); dielectric constant |
| $\epsilon_h, \epsilon$ | Electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, the potential of which is taken as zero (alternative symbols) |
| $\epsilon^0_h, \epsilon^0_c$ | Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration (alternative symbols |
| $\eta$ | Viscosity |
| $\theta$ | Temperature (centigrade), (alternative symbol) |
| $\kappa$ | Specific conductance (conductivity), magnetic susceptibility |
| $\Lambda$ | Equivalent conductivity |
| $\Lambda_{10}, \Lambda_v, \Lambda_\infty$ | Equivalent conductivity at different dilutions (volumes in litres containing 1 gram-equivalent) |
| $\Lambda_k, \Lambda_a$ | Equivalent conductivity of kation and of anion |
| $\lambda$ | Wave-length of light |
| $\mu$ | Molecular conductivity; magnetic permeability |
| $\pi$ | Ratio of circumference to diameter |
| $\Sigma$ | Summation |
| $\sigma$ | Surface tension (alternative symbol) |
| $\phi$ | Fluidity |
| $[\omega]$ | Specific magnetic rotation |

### *Remarks on the Symbols Recommended by the Working Committee.*

*Density.*—The symbol $\rho$ was suggested by the Electrotechnical Committee of Norway. The symbol $d$, with the alternative symbol $D$ to be used, for example, in the differential $dD/dt$, was adopted, as it is the initial letter of the name of the quantity in the different European languages and is also most generally employed by chemists.

*Volume.*—The Committee adopted $v$, $V$ as symbols for *volume* generally. The symbols $v_v$, $v_m$, &c., recommended provisionally by the International Commission in 1913 were omitted. In these and in other similar cases, the Committee considered that it was unwise to attempt to prescribe a definite symbol for every variation of the fundamental quantity. It was decided, therefore, to retain only the general symbol.

*Pressure.*—For reasons similar to those stated under "Volume," the Committee decided not to retain the symbol $P$ for osmotic pressure.

*Concentration.*—A number of suggestions were received for symbols for concentration expressed in different units. The Committee, however, considered that it was not advisable at present to adopt special symbols for such quantities. The symbols $c$, $C$ for concentration in general were therefore adopted, the author being left free to specify the units employed by him.

*Critical Quantities.*—The use of the Latin letters, recommended by the International Commission in 1913, was confirmed by the Committee. They were chosen in place of Greek letters, in accordance with a general principle adopted by the Commission that Greek characters should be used as sparingly as possible.

*Viscosity.*—The symbol $\eta$ was recommended by the Internationl Commission in 1913 as being in accordance with the usage among physicists. No objections to this symbol had been received, and the Committee confirmed its adoption.

*Surface Tension.*—The International Commission recommended the symbol $\gamma$ as chief symbol for surface tension on account of its employment in the classical researches dealing with this subject. No objections to this symbol had been received, and the Committee proposed that it should be retained, along with the alternative symbol $\sigma$.

*Diffusion Coefficient.*—The symbol $\Delta$ was suggested by the Spanish Chemical Society; the symbol $K$ by the Danish Chemical Society; the symbol $k$ by the American Chemical Society; and $D$ by the French Chemical Society. The Committee decided to recommend the symbol $\Delta$, which is but little used for other quantities (for example, depression of the freezing point), whereas $D$, $K$, and $k$ are used for the important quantities, density, equilibrium constant, and velocity coefficient of reaction.

*Equilibrium Constant.*—The symbol $K$, universally employed, was retained by the Committee. The Committee adopted the suggestion, made by the Danish Chemical Society, that, where necessary or desirable, the symbols $K_c$ and $K_p$ be employed for the equilibrium constant when molar concentrations and partial pressures respectively are employed.

*Degree of Dissociation.*—The International Commission in 1913 recommended the symbol $\alpha$ for the degree of electrolytic dissociation in preference to the symbol $\gamma$, as the latter is employed for surface tension and for the ratio of specific heats. The Committee agreed with this, and recommended that $\alpha$ be adopted generally for degree of dissociation (electrolytic, thermal, &c.).

*Entropy.*—For this quantity, the International Commission recommended the symbol $\phi$, on the grounds that this symbol was used by Willard Gibbs, and also because $S$ had been adopted for molecular heat. Obections, however, had been made to the use of $\phi$ by the Bunsen Gesellschaft and by the Russian Physical Society, and the symbol $\eta$ had been suggested by the American Chemical Society.

The Committee, after consideration, formed the opinion that although it is of importance to preserve, as far as possible, any symbol used in the classics of a science, reasons may exist for abandoning the classical symbol. In the present case, the symbol $S$ appears to be most largely employed by writers on thermodynamics, and has been adopted by the International Electrotechnical Commission. For this reason, the Committee adopted the symbol $S$, which has also the advantage that it is a Latin and not a Greek character. The use of $\eta$ as the symbol for viscosity is a further argument against the adoption of that letter as the symbol for entropy. The objection of the International Commission that $S$ was used for molecular heat no longer exists, according to the recommendations of the Working Committee.

*Specific and Molecular Heat.*—On the representations of the Bunsen Gesellschaft and of the Société de chimie physique, the Committee decided to recommend the adoption of the classical symbols $c$ and $C$ for specific and molecular heat in place of the symbols $s$ and $S$, which were recommended by the International Commission in 1913. The former symbols are those most frequently employed, and have been adopted also by the Ausschuss für Einheiten und Formelgrössen.

*Ratio of Specific Heats.*—The International Commission in 1913 recommended the symbol $\gamma$ in preference to $\kappa$ as being in growing use among physicists. The Working Committee confirmed this recommendation.

*Latent eat.*—The International Commission in 1913 recommended the generally employed symbols $l$ and $L$ for latent heat per grm. and per mole (grm.-molecule) respectivelly, the small and the capital letter being employed in accordance with general principles. The Danish Chemical Society suggested the symbol $q$ for (reversible) latent heat, and considered that it is not necessary to have different symbols for latent heat per grm. and per mole. That Society also raised objection to the use of the letters $l$, $L$ on the ground that they are, or may be, employed as symbols for solubility. The Working Committee, however, confirmed the recommendation of the International Commission for the following reasons: The letter $l$ is the initial letter of the distinctive part of the name of the quantity in the different European languages, and, further the symbols for latent heat and solubility would occur very seldom in the same formula.

*Maximum Work, or Diminution of the Free Energy of a System.*—The International Commission in 1913 recommended the symbol $W$ for "work." Whereas the Danish Chemical Society suggested that $W$ may be used as a symbol for "work generally," objections have been raised to the use of $W$ in the sense of "maximum work," or diminution of the free energy. Since it is the latter quantity that is of importance in physical chemistry, the Committee was of opinion that no symbol need be recommended for "work generally," and that the symbol $A$ should be adopted for "maximum work." This symbol has been adopted by the Ausschuss für Einheiten und Formelgrössen and by the International Electrotechnical Commission, and is used in the majority of text-books and journals. The American Chemical Society recommended the symbol $\psi$ $(=\epsilon - t\eta)$, the symbolism employed by Willard Gibbs. The Committee regretted that it felt it to be advisable, on the principle of disturbing existing usage as little as possible, not to adopt the Greek letters employed by Gibbs.

*Refractive Index.*—The symbol $n$ (with $n_\nu$ as alternative) was recommended by the International Commission in 1913 as being most generally employed. The Committee confirmed this recommendation. For the specific refractive power, according to Gladstone and Dale, and to Lorentz and Lorenz respectively, the symbols $r_G$ and $r_L$, or, if it is desired to indicate the temperature and wave-length of light, the symbols $[r_G]_\lambda^{t°}$ and $[r_L]_\lambda^{t°}$ were adopted as general symbols by the Committee. The use of $\lambda$ in this general symbol in place of $D$, given in the list of symbols recommended by the International Commission in 1913, seems preferable as being more general, and because $\lambda$ is the symbol for the wave-length of light. As a specific example, one might write $[r_G]_D^{18°}$.

*Molecular Rotatory Power.*—The Committee was of opinion that it is more in harmony with general principles to adopt the symbol $M[\alpha]$ for molecular rotatory power, and to redefine this as

$$M[\alpha] = \frac{\text{molecular weight} \times [\alpha]}{100} = [M].$$

*Magnetic Rotation.*—The Committee recommended the adoption of the symbol $[\omega]$ for specific magnetic rotation, and $M[\omega]$ for molecular magnetic rotatory power, which is defined in reference to that of water as unit

*Resistance.*—The Committee recommended the

adoption of the symbol $R$, which has been adopted also by the International Electrotechnical Commission. On the suggestion of the Bunsen Gesellschaft, the Committee adopted the letter $W$ as an alternative symbol for use when confusion with the gas constant may arise.

*Electrode Potential.*—The International Commission in 1913 recommended the symbol $\epsilon$ for electrode potential. Objections have been raised to the adoption of this symbol on the grounds that in writing, the Latin $e$ is frequently written like the Greek $\epsilon$, and also that the use of $\epsilon$, especially when the suffixes $h$ and $c$, for example, $\epsilon_h$, $\epsilon_c$, are added, is more trying to read. As the electrode potential is really an electromotive force, the Working Committee was of opinion that $E$, the symbol for electromotive force may also be adopted as chief symbol for electrode potential, the symbol $\epsilon$ being, however, retained as an alternative symbol.

*Dielectric Constant.*—The Committee decided to adopt $\epsilon$ instead of $\kappa$ as the symbol for this quantity, as the former had been adopted by the Ausschuss für Einheiten und Formelgrössen and by the International Electrotechnical Commission.

*Equivalent Conductivity.*—The adoption of the symbol $\Lambda$ was confirmed. It is defined as

$$\Lambda = \frac{1000\kappa}{\text{concentration in grm.-equivalents per litre}}$$

For the equivalent conductivity of the kation, the Committee considered that it is advisable to use the letter $k$ as suffix in place of $c$ (that is, $\Lambda_k$ in place of $\Lambda_c$), since the former letter represents a more correct transcription of the Greek, and is also largely used at present. The Committee recommended that kation should always be spelt with a k.

*Molecular Conductivity.*—The Committee recommended the symbol $\mu$

$$\left(= \frac{1000\kappa}{\text{concentration in moles per litre}}\right)$$

for the molecular conductivity. This quantity was not included in the list drawn up by the International Commission in 1913. It should be noted that this symbol should not be confused with that used by W. Ostwald for the molecular conductivity measured in reciprocal Siemens units.

ALEX. FINDLAY,
*Secretary to the Working Committee.*

## ATOMIC WEIGHT OF GERMANIUM.*

By JOHN H. MÜLLER

(Concluded from p. 61)

*The Apparatus.*—For obvious reasons the conversion of potassium fluogermanate to potassium chloride had to be effected in an all-platinum vessel, illustrated in Fig. 1. With slight modifications the weighing bulb and counterpoise were identical with those used by Smith and Van Haagen* in their recent determination of the atomic weights of boron and fluorine, in this laboratory.

The capacity of the long-necked platinum weighing bulb was 30 cc. The neck was 1·5 cm. wide, and the total volume of the flask about 40 cc.

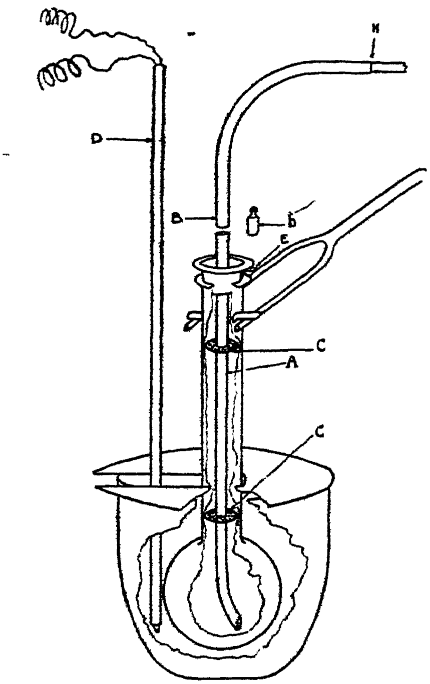


FIG. 1.

The inner tube A permitted the passage of the current of gas to the bulb and contents and was furnished with two perforated discs C. The discs were about 5 cm apart, and almost touched the walls of the neck of the flask. Their principal function was, of course, to prevent mechanical loss, but they also served to guide the inner tube into correct alignment for the adjustment of the platinum stopper, an important advantage because of the delicate nature of a ground platinum connection.

The bulb was supported upon two stout arms or lugs near the top of the flask and diametrically opposite each other. These rested upon the platinum-covered prongs of a fork projecting from a stand (not shown).

B shows the platinum elbow-tube, the end of which was ground to fit the entrance to the inner tube. A small platinum stopper ground to the same size ($b$) served to close the inner tube during weighing.

A large platinum crucible and perforated cover prevented direct contact of the bulb and flame; and as the temperature during each determination had to be controlled, a platinum-iridium thermocouple, D, was introduced through the crucible cover, the end of the couple being on a level with the bottom of the weighing bulb.

The waste hydrogen chloride bearing the decomposition products, germanium and tetrachloride and hydrogen fluoride, was taken off through a pure gold cap and tube G (shown in Fig. 2), and drawn through large wash-bottles containing water and caustic soda solution. The cap fitted loosely over the entire top of the flask during the

*From *Journal of the American Chemical Society*, May, 1921.

use of the hydrogen chloride but was not required while the nitrogen and air were in use. These latter gases were simply allowed to escape into the air around the stopper, which was slightly raised from its seat by means of a small piece of platinum foil inserted at E (Fig. 2). Thus the neutral gases were thrown away, but excess of acid gas was disposed of and its germanium content recovered without complicating the apparatus further by adding a side arm and stopper.

The generators and entire systems for washing and drying of air, nitrogen and hydrogen chloride were constructed wholly of glass, all connections between washing bottles being fused together, and ground connections were only used between

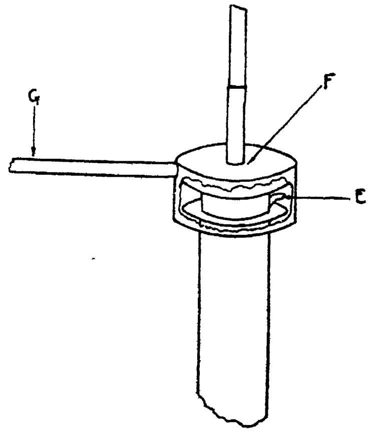


FIG. 2.

generator flasks and the anterior ends of the washing trains. These three gases passed to a three-way stopcock from which any one gas could be taken off through a single supply tube leading to the platinum connection H. The connection between glass and platinum at H was a carefully ground joint and a very tight connection was effected at this point by first grinding the glass and platinum to accurate fitting, heating the platinum and then slipping it while hot on to the cooler glass. Upon cooling and contracting, the softer platinum took fast hold and the joint remained gas-tight throughout all determinations.

The apparatus proper (excepting only the gas generators and washing systems), was enclosed in a large glass-sided cabinet furnished with a tight sliding door and a small opening at the top for the escape of hot air. This precaution was important on account of the many hours of exposure of the bulb for a single determination and served admirably to exclude dust and laboratory fumes from the vicinity of the weighing bulb.

Manipulation of the bulb and counterpoise adjustment of platinum connections, &c., were facilitated by the use of four thoroughly washed and lint-free linen finger covers. These allowed a much firmer hold of the flask and more accurate adjustment of stoppers than the usual use of tongs or handkerchief. They were kept ready for use and free from dust in a compartment of the dessicator used for the bulb and counterpoise.

*Balance and Weighing.*—Weighings were made were made on a Troemner balance No. 10, which is easily sensitive to 0·02 mg. The weights were carefully calibrated by Richards' substitution method. The larger weights were of gold-plated brass and the fractions of platinum. The counterpoise was a platinum flask of nearly the same weight and surface as the weighing bulb. Both bulb and counterpoise were allowed to come to the same temperature and surface condition side by side in a large dessicator, and the dessicator was allowed to remain near the balance for some hours before final weighings were taken.

For vacuum corrections, 1·995 was taken as the accepted density of potassium chloride (*Journ. Am. Chem. Soc.*, 1907, xxix., 632). The density of potassium fluogermanate had to be determined. For this purpose pure toluene distilled over sodium and redistilled alone was used. The mean of three determinations at 22° was 3·244. The corrections were of quite appreciable magnitude, amounting to +0·00045 per grm. of chloride and +0·00024 per grm. of fluogermanate.

The atomic weights used in calculating the atomic weight of germanium were chlorine, 35·46; potassium, 39·10; and fluorine, 19·00.

*The Dehydration of Potassium Fluogermanate.*

It is known that the removal of water from a number of double fluorides is accompanied by partial decomposition, small amounts of oxygen being introduced into the salt with the elimination of some hydrofluoric acid. As such decomposition would introduce serious error into exact determinations, the proper conditions for dehydration of the fluogermanate were studied in preliminary experiments.

A 15-g. sample of the moist centrifuged purest potassium fluogermanate was allowed to dry in dust-free air at room temperature. 4·50071 g. of this air-dried sample was then exposed to a slow current of perfectly dry air for six hours at 70° to 80°. The loss in weight was 0·00035 g. When further exposed to dry air at 450° the weight became constant after a loss of 0·00810 g. Reheating for 14 hours at the same temperature afforded no further loss. The salt then weighed 4·49128 g.

Another portion of the original air-dried salt was exposed *in vacuo* over sulphuric acid for nearly a week, when the moisture content was only slightly changed. It was then evident that the small quantity of water in the salt was enclosed within the crystals and could not be removed except at a temperature at or near the melting point. As mentioned before, the melting point of the salt is over 700°, but at that temperature it is appreciably volatile. At 450° no volatility could be detected. It seemed advisable, therefore, not to use a temperature higher than 450°; but as the long-necked flask and its perforated discs acted as a condenser, it was possible after a preliminary drying at 400° to 450° to stop the air current and raise the bottom of the flask to a higher temperature for a few moments without loss. The salt then sintered together but did not lose more weight. Accordingly the conclusion was drawn that a temperature of 450° and a slow current of air will completely dry the salt if time enough be allowed. At higher temperatures it is evident that the condensation of sublimed salt upon the obstructions well up in the neck of the flask would have introduced a greater error than the possible trace of moisture that might have been left in the salt dried at 450°.

A much higher temperature was used, of course, to melt the residual potassium chloride, but this operation was not necessary until all of the germanium and fluorine had been removed in hydrogen chloride.

*Final Determinations.*

The general procedure in the dehydration of the potassium fluogermanate was the same in all determinations, and may be outlined as follows.

The empty bulb, protected by the platinum crucible air-bath, was ignited at 800° for about 20 minutes, and a current of dry air was allowed to pass through tht bulb during the application of heat. It was reweighed to constant weight ±0·02 mg., approximately The sample of fluogermanate was then introduced through a platinum funnel, the stem of which projected well down into the neck of the flask. The bulb was then connected with the air supply and a slow current of dry air was passed through at 60° to 70° for three hours, then at 150° for two hours, and then the temperature was raised slowly to 400° to 450°, and so maintained for four to six hours. More than three reheatings at 400° were seldom required to give a weight constant to 0·02 or 0·03 mg.

The weighing bulb was then connected with the supply of hydrogen chloride, and this gas was allowed to act on the dry salt, at 100° to 150° for three hours, during which time the major portion of the germanium passed off Several cubic centimetres of water was now introduced into the bulb (except in the first determination), and the aqueous mass was then carefully heated to 70° or 80° in the same gas until practically all of the water was removed. The initial partial drying took about six hours. The temperature was then elevated slowly to about 500° for a short period, and finally to the melting point of the residual chloride. The bulb was allowed to cool, water was again introduced, and the process outlined above was repeated. A third introduction of water, and repetition of the drying process was carried out in the last four determinations. The residual chloride was then raised to 600° in the presence of hydrogen chloride, and most of the latter gas was removed in a current of nitrogen at that temperature. The passage of nitrogen was continued for some time, and the chloride was finally brought to fusion. The temperature was then lowered, and the nitrogen swept out of the bulb by passing in a slow current of air for several hours. This gave the first weighing of the chloride. The entire operation described above was then repeated and carried out to obtain a constant weight of the chloride. The long time required for the complete expulsion of all of the hydrogen chloride made it advisable to prolong the first treatment with this gas far in excess of the actual time required for the conversion of the fluoride to chloride. In Determination No. 1 the operation was made entirely in the dry way. Five reheatings in hydrogen chloride were needed to arrive at constant weight within the limit of 0·04 mg. Hence the other determinations were all carried out with the use of the acid gas in the presence of water and the length of time of exposure to the acid was greatly increased to bring about the removal of the added water before high temperature was applied. It need hardly be mentioned that after the introduction of water into the bulb, evaporation was carried to nearly complete dryness at a temperature below 100°.

One determination was lost because of the introduction of water into the bulb before the most of the germanium had been expelled in dry hydrogen chloride, the trouble being then caused by the sudden elimination of germanium along with water vapour. A deposit of germanium oxychloride was thus produced, which collected upon the upper portions of the neck of the flask and the stopper. As this part of the flask could not be properly heated and was in contact with air at all times, this determination was not carried further.

In the other six determinations, the dry fluogermanate was treated with dry hydrogen fluoride at 100° to 150° for some hours before any water was used to decompose the residual chloride and fluoride mixture. The water was added in just about sufficient quantity to dissolve the entire residue in the cold.

Results of the seven determinations are given in the table below.

| Determination | Weight of potassium fluogermanate *in vacuo.* G. | Weight of potassium chloride *in vacuo* G. | Atomic weight of germanium K=39.10. Cl=35.46. F=19.00. |
|---|---|---|---|
| I. | 1·94831 | 1·09814 | 72·37 |
| II. | 3·09380 | 1·74350 | 72·41 |
| III. | 2·10784 | 1·18774 | 72·44 |
| IV. | 2·36113 | 1·33044 | 72·44 |
| V. | 4·38070 | 2·46863 | 72·42 |
| VI. | 1·52575 | 0·85970 | 72·45 |
| VII. | 4·00100 | 2·25483 | 72·40 |
| | | Mean | 72·418 |

*Summary.*

The results and conclusions derived from the preceding investigations may be summarised as follows.

1. The processes of purification of the germanium salt used for the determination of the atomic weight of this element embodied a more thorough treatment for the elimination of the known impurities of germanium than previously reported.

2. The chlorine-hydrochloric-acid distillation process, though adequate for the removal of silica and tin can hardly be accepted as a means of eliminating the last traces of arsenic from germanium compounds Four redistillations of the chloride from hydrochloric acid solution in a stream of chlorine failed to remove the last of the arsenic.

3. The treatment of the nearly pure germanic oxide with sufficient water to dissolve nearly all of it, and the fractional crystallisation of the hydrated oxide from this solution served a two-fold purpose, to remove the much more soluble arsenic oxide at one end, and to remove any remaining traces of tin and silica in the less soluble fractions at the other. It should be noted that the formation of the potassium fluogermanate was not carried out until the absence of the isomorphous fluostannate and the silicate was insured by complete removal of tin and silica from the original oxide.

4. The stability of the final product, potassium fluogermanate, and the anhydrous nonhygroscopic nature of this salt, together with its complete decomposition in hydrochloric acid seemed to indicate that it was the most favourable compound of germanium for accurate analysis. The complete

conversion of the salt to potassium chloride was in every case established by negative tests for both germanium and fluorine.

5. The mean of seven determinations of the ratio of potassium fluogermanate to the potassium chloride equivalent gave 72.418 for the atomic weight of germanium, calculations being based on the assumption that chlorine is 35·46, fluorine, 19·00, and potassium, 39·10.

In conclusion, the above investigation suggests that an examination of other double halides of germanium and the alkalies might give desirable compounds for accurate analysis by a similar volatilisation of the germanium content, and thus furnish a check upon the results obtained in this work.

## UNIVERSITIES, RESEARCH, AND BRAIN WASTE.*

By J. C. FIELDS, Ph.D., F.R.S.

(Continued from p. 63)

In America there are no recognised safeguards for the professoriate such as exist on the other side of the Atlantic. There are no traditional standards by which the candidate for a professor's chair must qualify. It is not always a question of scientific achievement. Local pull is frequently in evidence. Executive and committee work within the university and outside activities with an advertising value often receive their reward. Where, too, it is the intention of the appointing power to make the scientific status of a candidate the determining factor the scientific advice invoked is often far from competent. Some years ago the American Mathematical Society, recognising the existing state of affairs, named a committee to consider whether it might not be possible to bring the knowledge and experience of the Society to bear in the making of mathematical appointments in universities and colleges The committee, however, reported that they were unable to devise any means for attaining the desired end.

The material which goes to make up the teaching staff of an American university is most heterogeneous. Not all the young men who enter the academic profession are of the idealistic type to which I have referred a little earlier. Their average, however, would compare favourably, I think, with the average in any other walk of life. They all look forward to professorships, of course, and one or all may ultimately arrive. Promotion in an American university is slow. The gradations leading up to a professorship are more numerous on this side of the Atlantic than in Europe. Though the scientific qualifications in America are on the whole less exacting than in Europe, advancement, for the man of ability at least, is not as rapid. The man of high attainments will find himself a professor at an earlier age in Europe than in America. However it may be in other departments of human activity, America is not the land of the young man in the field of academic work.

I have taken occasion to speak of the overloading of members of the American universities' staffs with teaching. This had reference to the professors in general as well as to the junior members of the staffs. The number of lectures which a professor in an American university is called on to give is much in excess of that demanded of his European compeer. In response to a question of mine as to the number of lectures which he was expected to give in the course of a year, a professor on the staff of Oxford told me that his position required him to lecture 28 hours in the course of the year. As a matter of fact, however, he lectured 56 hours. In France, a professor is expected to lecture three hours a week. This is usually for the academic year of 30 weeks, though some of the professors in Paris are only required to lecture 15 weeks. In Germany it is stipulated that the professor lecture at least two hours a week throughout the academic year. He, usually of his own volition, gives more than the stipulated number of hours He is not troubled by the limitations of a fixed curriculum, it may be noted. He lectures on subjects of his own choosing, and rarely on more than two at a time.

In America it is nothing out of the ordinary for a professor to give 300 to 500 lectures in the course of a year. The layman may fancy that this is not too much, and he is likely to jump to the conclusion that the European professor has a very easy time of it. Let us see, however, how it works out. The European professor is in a position to concentrate on one subject at a time. It may be that the literature on the subject is not organised up to date. For the purpose of his course of lectures it will be necessary to organise it. To digest and collate the scattered material is likely enough to be a task of some magnitude. It will probably be as much as he can handle. It may be that it will take him several years to do the work. Here and there, by the way, he may delay over a point which needs to be cleared up or a problem whose solution would be useful. However that may be, one result of his labours will, as likely as not, be a treatise which will be of service to many more individuals than he could reach by word of mouth in the class-room. These individuals would be located in different countries and distributed over the surface of the civilised earth, including among them seasoned research workers as well as immature students. Occasionally, too, the lectures of a creative thinker will consist largely in the exposition of successive discoveries which he is making in the course of the development of a subject.

The lectures of an American university professor will rarely be of the character of the lectures to which we have just referred. They can not have such character if they are to run into the hundreds annually. As a matter of fact, many of the so-called lectures in universities on this continent consist entirely of text-book work, and are purely tutorial in their character. This is necessarily the case in institutions which are half high school and half university.

The typical American professor who lectures on a multiplicity of subjects simultaneously can hardly concentrate on any one of them. He certainly cannot concentrate on all. He has to be perpetually changing interest as he jumps from one subject to another. He has to be content with placing himself in position from day to day with regard to the successive parts of the several subjects, and the position in which he places himself is pretty much the same from one year to another

*Reprinted from the *Transactions of the Royal Canadian Institute* February 1921.

so that the same lectures are repeated from year to year and finally become a matter of routine.

The lecturer who concentrates on one subject at a time, and changes that subject from year to year or at longer intervals, covers a much larger territory in the end than the man who drives the same half-dozen subjects abreast year after year. Besides this, he has a much better command over his material. The conditions best adapted to the needs of a scientist, the conditions under which he will attain his maximum as a research worker, and prove himself most efficient as a teacher, are not always clearly apprehended by American university administrations.

The American university is administered by a Board of Regents composed wholly or almost wholly of business men. There is a President appointed by the Board and appointments to the teaching staff are made by the Board on the recommendation of the President. In general the Faculty has no representation on the Board and its sole connection with the Board is through the President. There is a good deal of dissatisfaction with this arrangement, I was told while on a visit to the United States last summer. A prominent member of the academic staff of one of the principal American universities gave expression to this feeling by stating that the teaching staff was slave to the administration. There have been some experiments in the way of modifying the organisation. Representation of the Faculty on the Board of Regents has been tried. There have also been committees of the Faculty having access to the Board, and committees composed of members of the Board and members of the Faculty. With what success these tentatives have met I do not know. There does not seem to be complete unanimity with regard to the remedy which is needed for the existing state of affairs. I may say that in European universities there is no administrative body of the nature of the Board of Regents of an American University, and there is no office which corresponds to that of the American university President. The principal of a British college or university has nothing like the powers of the university President. The Faculty has far more influence in the conduct of affairs than is the case in America. This is in evidence in the making of appointments For example, where the system of electors is in operation the Faculty has a voice in choosing the electors. It also has its say in the case of universities where the system of electors has not been adopted.

In our Canadian universities we have the American form of administration. Our curriculum and academic standard, however, have been imported from Great Britain. We have adopted the idea of the honours courses, and these courses at the University of Toronto are probably the heaviest undergraduate courses on the continent. With this foundation one would have said that we should have developed along graduate lines more rapidly than has been the case. Some of the American universities, however, have greatly outdistanced us in the development of graduate and research work. Let us hope that we shall overtake them. Our students who have received their bachelor's degree in one of the honours courses compare more favourably as a rule with those who have completed an undergraduate course in the corresponding department of an American university. The result of a comparison with the best product of the universities on the other side of the Atlantic is, however, not so favourable. The conception of a university at its best is on a somewhat higher plane in Europe than in America. The same is true also of the secondary school. A young man of exceptional ability being trained in Europe is likely to be somewhat in advance of where he would find himself at the same age if he were being trained in America. On entering Oxford or Cambridge, a student specialising in mathematics is about two years ahead of a student entering the University of Toronto in the same department, while he is just one-year older. The discrepancy in classics is quite as great. This does not hold in case of the natural sciences, which receive less attention than mathematics and classics in the Public Schools of England. From what we have just said, however, it would appear that it should be possible to so modify the methods of instruction in our Canadian secondary schools as to save a year to our brighter boys by the time they are ready to matriculate. A comparison with results obtained on the continent would lead to the same conclusion.

The university attendance in the Province of Ontario in proportion to population compares favourably with that of any other country except Germany, after all due allowance has been made for inequality of university standards in different countries. Nevertheless, six out of seven pupils who pass the High School entrance examination never matriculate. About seven out of nine do not attempt the matriculation examination. (The figures here given are based on the results for the matriculation examinations during the five years 1910-14, and on the results for the High School entrance examinations during the five years 1906-1910). Among these boys and girls there are sure to be many who would profit by a university course. Much good material must here go to waste. Why should we not have in Ontario, or better still throughout Canada, a system of scholarships which would provide the highest possible education for the exceptionally gifted? Australia makes such provision for her gifted boys and girls. Why should we do less for ours?

(To be continued)

## AN APPEAL
### BY MERCHANTS, MANUFACTURERS, AND SHIPOWNERS OF THE UNITED KINGDOM.

WE have received from the National Association of Merchants and Manufacturers the following notice, together with a list of over 800 signatures, which appears to include most of the chemical manufacturers in the Kingdom :—

"We, the undersigned Merchants and Manufacturers of the United Kingdom, desire to endorse the weighty Appeal by leading Bankers issued on May 12, and to insist with them on the need of dealing promptly with the perilous situation in which the country is placed.

"The Appeal, which opens by recalling the Petition of the Merchants of the City of London addressed to the House of Commons in 1820, dwells on the parallel between the state of the country then and now.

"At the present juncture the following problems

seem to call most urgently for attention :—

An immediate and drastic reduction of expenditure is of vital importance

The freeing of our trade and industry from the trammels imposed by the War is not less essential.

The interference with our commerce, whether by Parliament or by the Administration, must be stayed at once.

But it is perhaps even more important that the inhabitants of this country should be impressed with the absolute need for greater industry and greater thrift, so that the wealth annihilated by the War may be restored. Such restoration can only be accomplished by earning more and spending less.

"By these means alone shall we be able to bear the burdens from which we suffer, to regain the foreign trade essential to our prosperity, and to contribute to the well-being, not only of our own country, but of all other countries on which we are largely dependent.

"We invite our fellow-countrymen to join with us in impressing on the Government, on Parliament, and on the nation at large, the paramount importance of these great questions."

# PROCEEDINGS OF SOCIETIES.

## FARADAY SOCIETY.

*June* 22, 1921.

Prof. A. W. Porter, F.R.S., President, in the Chair.

"*High Temperature Phenomena of Tungsten Filaments.*" Part I. By C. J. Smithels (for the Research Staff of the General Electric Co).

Two types of tungsten wire are in general use for lamp filaments One is composed of pure tungsten, and the other of tungsten containing up to 1 per cent of a refractory oxide such as thoria. The crystal growth during burning has been investigated for both types. It is shown that the deformation of the filament which occurs during life is a function of the crystal growth. Crystal growth, which is suppressed in thoriated filaments occurs when the thoria is reduced. Thoria, and other refractory oxides, can be reduced by phosphorus vapour at a high temperature.

Part II. Deals with the chemical reactions which occur in gas-filled tungsten filament lamps when traces of the common gases are present in the filling gas. The types of failure which are produced in each case are described. The paper was illustrated by photomicrographs.

"*A Simple Apparatus for Determining the Coagulations Velocity of Gold Sols.*" By Emil Hatschek.

The percentage of blue formed in coagulation of red gold sol is taken as a measure of the degree of coagulation. The percentage is determined by comparing the original red sol with a double wedge, one half consisting of the original sol, and the other of the completely coagulated blue sol It is necessary that the latter should be coagulated by the same electrolyte as that used in the sol under examination, as the blues obtained with different electrolytes are not exactly alike. A number of determinations have been compared with V. Smoluchowski's formula for the coagulation velocity, and show good agreement for complete and fairly rapid coagulation.

The President then read a paper on the "*Variation of Surface Tension and Surface Energy with Temperature.*"

"*The Influence of Solvent upon Ionisation and the Accompanying Heat Effects.*" By S. M. Neale.

A determination by electrical conductivity methods of the ionisation of picric and paranitrobenzoic acids in mixtures of acetone and water. From the values obtained at 25° and 35° C., the heats of ionisation are calculated. In the case of picric acid, the heat of ionisation varies largely with the nature of the solvent, passing through a minimum at about 70 per cent acetone. In the case of paranitrobenzoic acid the heat of ionisation is sensibly zero both in water and in 44 per cent acetone, although in the latter solvent the ionisation constant has fallen to one-twentieth of its value in pure water as solvent.

"*The Potention of the Iodine Electrode and the Activity of the Iodide Ion at* 25° *C.*" By A. McKeown.

The potential of the saturated iodine electrode in combination with the normal calomel electrode has been measured for various values of the concentration of the iodide ion. The results have been compared with those of other investigators, making use of the concept of activity coefficient, the activities of the iodide and of the tri-iodide ion in the various solutions have been estimated and compared with the values of the concentration of these ions. It is found that the activities of both ions increase less rapidly than their concentrations. From the results the normal potential of the iodine electrode is calculated to be +0·2454 volts, the normal calomel being taken as zero.

# CORRESPONDENCE.

## ETHYLSTANNIC ACID.

*To the Editor of the Chemical News.*

Sir,—In reply to Mr. Redgrove's letter in your issue of July 15, dealing with the nomenclature of the compound $C_2H_5.SnO.OH$, I wish to point out that the name *ethylstannic acid* is that adopted by the Chemical Society, and it does not meet with my own approval, as the reactions of the substance indicate that it is a compound of bivalent tin.

In a paper contributed a short time back to the Chemical News, on the corresponding methyl compound, I termed the substance methylstannic acid, following the nomenclature adopted in the abstracts of the Chemical Society's *Journal*, 1903, i., 470, and 1903, i., 802. The Chemical Society now favour the nomenclature criticised by Mr. Redgrove, viz., ethylstannic acid for the compound $C_2H_5.SnO.OH$; see also *Journal Chemical Society*, Abstracts, 1910, i., 724. This is to be regretted, since the bivalent nature of the tin in this class of substances is thereby obscured.—I am, &c.,

Gerald Druce.

## NOTES.

Institute of Chemistry.—*Pass List.*—The following candidates have been successful in the July, 1921, Examinations, and have been duly elected Associates of the Institute:—Examination in General Chemistry: Campbell, Alan Newton, B.Sc. (Lond.); Doolan, James Joseph; Evans, Benjamin Beardmore, B.Sc. (Birm.); Hand, George Percy Terry; Jenkin, John Watson; Pugh, William; Ridge, Bert Pusey; Woolf, Sidney Samuel, B.Sc. (Lond.). Examination in Metallurgical Chemistry: Storer, George Paterson. Examination in Organic Chemistry: Kenyon, Frank; Sheldon, Francis Joseph, A.R.C.S., B.Sc. (Lond.). Examination in the Chemistry of Foods and Drugs, &c.: Martin, Charles William; Mooney, Paul Michael, B.Sc. (Lond.); Woodward, Miss Elsie. Examination in Chemical Technology (Soap, &c.): Smith, David Dow; (Coke Oven Practice, &c.): Whitaker, John Wilfrid, B.Sc. (Lond.).

Wages and Employment.—The serious nature of the depression and the effect of the coal stoppage which lasted throughout April, May, and June, may be measured by the extent to which employees have been thrown out of work or placed on short time. The following figures, which cover all classes of workpeople, but do not include coal miners, show the number of persons on the Live Registers of the Employment Exchanges on the dates given:—

| | |
|---|---|
| December 31 | 756,823 |
| January 28 | 1,065,320 |
| February 25 | 1,218,218 |
| March 25 | 1,413,751 |
| April 29 | 1,854,059 |
| May 27 | 2,122,496 |
| June 24 | 2,178,000 |

The increase in the March figure over that for February is chiefly due to the re-registration of applicants who became entitled to a further period of benefit under the Unemployment Insurance Act which came into operation on March 3. The number of unemployed persons insured under the Unemployment Insurance Acts, 1920 and 1921, and the number of short-time workers in receipt of benefit on certain dates, together with the corresponding figures for December 31, are given below:—

| Date. | Totally Unemployed. | On Short Time |
|---|---|---|
| December 31, 1920 | 433,571 | 435,152 |
| March 25, 1921 | 1,194,000 | 744,000 |
| June 24, 1921 | 1,971,192 | 758,429 |

The Trade Union figure of unemployment, which is based on reports to the Ministry of Labour by Trade Unions with an aggregate membership of 1¼ millions, shows the following fluctuations:—

| | Per cent. | | Per cent. |
|---|---|---|---|
| January | 6·9 | April | 17·6 |
| February | 8·5 | May | 22·2 |
| March | 10·0 | June | 23·1 |

The corresponding figure for July, 1914, was 2·8 per cent, and the average for 1920 2·4 per cent.—*Board of Trade Journal.*

Tenders Invited for Disinfectant.—The Municipal Council of Johannesburg invites tenders to be presented with samples not later than noon on September 1 next, for a six months' or, alternatively, twelve months' supply of fluid disinfectant. The approximate annual requirements of the Council are given as 5,000 Imp. gallons in drums containing 5 Imp. gallons. A copy of the specification, tender form, general and special conditions of tender, is available for inspection by United Kingdom manufacturers and suppliers on application at the Enquiry Room of the Department of Overseas Trade, 35, Old Queen Street, Westminster, S.W.1.—Department of Overseas Trade

## NEW COMPANIES.

The under-mentioned particulars of New Companies recently registered are taken from the Daily Register compiled by Jordan & Sons, Limited, Company Registration Agents, Chancery Lane, W.C 2.

Nagels & Co. (London), Limited.—(175639)—Registered July 9th, 1921. 76a, Chancery Lane, W.C.2. To carry on the business of General Merchants, Chemists, Druggists, Drysalters, etc. Nominal Capital: £1,000 in 1,000 Shares of £1 each Directors: V. G. Van Waasdyk, Malden Hall, Watford (Chairman and Managing Director), G. C. Gagan, 109, Inville Road, S.E.17. Qualification of Directors: £1. Remuneration of Directors: To be voted by Directors.

Egerton Chemical Company, Limited.—(175613)—Registered July 8th, 1921 19, Brazennose Street, Manchester. To carry on the business of Manufacturing Chemists. Nominal Capital: £1,000 in 1,000 Shares of £1 each. Directors: J. F. Key, 32, Oak Road, Higher Crumpsall, Manchester; A Ferrie, 122, Lansdowne Road, West Didsbury, Manchester. Qualification of Directors: 1 Share. Remuneration of Directors: To be voted by Company.

Manchester and District Radium Institute.—(175725)—Registered July 14th, 1921. Nelson House, Nelson Street, Manchester. To acquire Radio-active Materials whether containing Radium or Mesothorium or other Radio-active Substances of any description. Every Member to contribute a sum not exceeding £1 if necessary. Directors: Sir E. Holt, Woodthorpe, Prestwich; Sir W. Cobbett, Woodlands, Wilmslow; F. P. Nathan, Crumble Lodge, Swinton Park, Pendleton; G. M. Midwood, The Grange, North Road, Congleton; L. Pilkington, Firwood, Alderley Edge, Sir W. Milligan, Westbourne, Rusholme, Manchester; S H. Renshaw, Beech Grove, Chesham Bury; W. Armitage, Barthomley, Catherine Road, Bowdon.

T. H. Smith (Wisbech), Limited.—(175644)—Registered July 9th, 1921. 1, Market Chambers, Market Street, Wisbech. To carry on the business of Agrihorticultural Chemists, Manufacturers and Dealers in Pulp, Jam and Preserves. Nominal Capital: £500 in 500 Shares of £1 each. Directors: T. H. Smith, 29, West Street, Wisbech; R. Scrafton, 1, High Street, Wisbech. Qualification of Directors: £1. Remuneration of Directors: To be voted by Company.

Catalytic Chemical Company, Limited.—(175760)—Registered July 16th, 1921. To carry on the business of Manufacturing Chemists and Druggists. Nominal Capital: £10,625 in 10,000 Preference Shares of £1 each and 25,000 Ordinary Shares of 6d. each. Minimum Subscriptions: 7 Ordinary Shares. Directors: W. H. Collbran, Elmley, Park Side, Wimbledon Common; J. Day, Derwent House, Wimbledon Park Road, S.W.19.; W. R. Walkey, 52, Upper Richmond Road, East Sheen. Qualification of Directors: 100 Shares. Remuneration of Directors: £100. Chairman: £200.

Leighton Laboratories, Limited.—(175834)—Registered July 20th, 1921. To carry on the business of Manufacturers of Chemicals of all kinds. Nominal Capital: £5,000 in 4,900 Cumulative and Participating Preference Shares of £1 each and 2,000 Ordinary shares of 1/- each. Directors: C. E. Bergin (Managing Director). Qualification of Directors: £100. Remuneration of Directors: To be voted by Company.

Barker Brothers (Simpson Clough), Limited.—(175757)—Registered July 16th, 1921. Simpson Clough Mill, Heywood, Lancashire. To acquire and carry on the business of a Bleacher Dyer and Finisher. Nominal Capital: £70,000 in 70,000 Shares of £1 each. Directors: P. V. Barker, Simpson Clough, Heywood; F. Barker, Simpson Clough, Heywood; E. Barker, 149, William Street, Heywood; H. Barker, Springfield, Hopwood, Heywood. Qualification of Directors: 50 Shares. Remuneration of Directors: To be voted by Company.

W. A. Wilson & Sons, Limited.—(175870)—Registered July 21st, 1921. To acquire and carry on the business of Chemical and Colour Merchant. Nominal Capital: £4,000 in 4,000 Shares of £1 each. Directors: C. Collins, 36, Leysfield Road, Hammersmith, W; W. A. Wilson, St. Breock, Vicarage Road, Woodford Bridge, Essex; P. Wilson, St. Breock, Vicarage Road, Woodford Bridge, Essex; A C. Stevens, School Green, Freshwater, Isle-of-Wight. Qualification of Directors: £500. Remuneration of Directors: £100 each.

## New Patents.

This List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W.C.2, from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

19053—Aitchison, L.—Purification of chromium ores and residues containing chromium oxides. July 14.
18949—Allsebrook, W. A.—Manufacture of lead chromate pigments. July 13.
19217—Cooper, C.—Manufacture of sulphate of ammonia. July 16.
18806—Klencke, H.—Process for production of sulphuric acid. July 12.
19220—Marr, J.—Manufacture of benzanthrone derivatives July 12

*Specifications published this Week.*

128939—Nitrogen Corporation.—Process of synthesizing ammonia.
166036—Heisch, G. P.—Ammonium sulphate saturaters.

*Abstract Published this Week.*

*Glycerine.*—Patent No 164034—An improved process of producing glycerine has been patented by Mr. A. T. Hocking, Carhampton House, Four Oaks, Sutton Coldfield, and Lily C. H., 29, Carlyle Road, Edgbaston, Birmingham, both in Warwickshire. The glycerine is produced by fermenting sugar solutions containing a mixture of about equal weights of alkali bisulphite and sulphite. The mixed sulphites may be added in successive small quantities to a proportion corresponding to the percentage of glycerine desired, the proportion of acetaldehyde and alcohol being greater the less proportion of sulphide; and the liquid may be maintained approximately neutral by successive additions of alkali bisulphite solution or by increasing the proportion of bisulphite in the additions of the mixed sulphites. In an example in which the maximum glycerine yield was required, 311 gallons of a solution of crude cane sugar, equivalent to 788 lb glucose were fermented by 40 lb. of yeast at a temperature of 35-37° C for 9 days, and during the first five days 176 gallons of mixed sodium sulphite and bi-sulphite solution equivalent to 545 lb. $Na_2SO_3$ were added in doses, first of 40 lb. and then of 30 lb. mixed salts in 16 gallons of water. In this way, 336 lb. glycerine, 172.2 lb. of acetaldehyde, and 37.4 lb. alcohol were produced.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.



## NOTICES.

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THE CHEMICAL NEWS.
VOL. CXXIII., No. 3200.

## NOTE FROM THE EDITOR.

NOW that the dislocation of work is over, and the readjustment of effort brought about by the death of Sir William Crookes has in great measure become permanent, the writer, whose connection with Sir William is tolerably well known, has decided to collect together and complete some notes and enquiries that were under consideration during the last few years of work in the Laboratory at Kensington Park Gardens. The following is the first of such notes, and others will follow in due course.

ABSORPTION OF HEAT BY SOLUTIONS. For the Microscopic Projection Apparatus. (From the Private Notes of the late Sir WILLIAM CROOKES).

Some little time ago I had occasion to project on a screen images of sections of crystals and microscopic objects mounted in Canada balsam. The objects had to be highly magnified so as to be seen on a 20ft. screen, and it was necessary to concentrate a strong beam of electric light on the object. Several slides were destroyed by the Canada balsam boiling and charring, and experiments were then instituted to see if solutions could be found that would transmit sufficient light without risking injury to the object by too great heat.

The projection apparatus was fitted as for an experiment, and instead of an object, the blackened bulb of a thermometer was introduced With no liquid intervening, the thermometer would have been destroyed at once, for the heat was sufficient to ignite cloth, brown paper, and wood. A glass cell, 50 mm. from back to front, was accordingly interposed, and various liquids were filled into it. The arc was kept as constant as possible, and the beam tempered by the liquid was allowed to play on the bulb of the thermometer for ten minutes. The maximum temperature was reached in two or three minutes.

The following Table gives the strength of the different solutions employed, and the maximum height attained by the thermometer.

| Solutions employed | Temperatures recorded. |
|---|---|
| Distilled water | 197° C. |
| Ammonia alum, saturated solution | 170° C. |
| Ammonio-ferrous sulphate, 3oz. to the litre | 143° C. |
| Ferrous sulphate, 3oz. to the litre | 138° C. |
| Copper sulphate :— | |
| ⅛oz. to the litre | 118° C. |
| ¼oz. to the litre | 104° C. |
| ½oz. to the litre | 93° C. |
| 1oz. to the litre | 87° C. |
| 2oz. to the litre | 80° C. |

From this Table it is seen that water and solutions of alum are very poor obstructors of heat, sufficient getting through to injure a microscopic slide in the focus of the beam. Copper sulphate solution is a good interceptor for radiant heat, and it can be used safely as weak as ⅛oz. to the litre, at which strength the colour is almost imperceptible on the screen with ordinary objects, and it does not much interfere with the colours in polarisation experiments with crystals, while the comfort of using a concentrated beam of electric light on the object with no fear of injuring it is worth a slight diminution in the brilliancy of the colours.

## NICKEL ISOTOPES.

By F. H. LORING.

IN view of Aston's recent announcement in *Nature* (June 23, 1921) that nickel has isotopes of masses 58 and 60, I hereby amend a portion of the Table given in the CHEMICAL NEWS (August 27, 1920), to read as follows :—

| Elem't. | $n \times$ He | *a* | *b* | *c* | *d* | | Isotopes & Prop. No. | 'Calc.' & Exp Mass. |
|---|---|---|---|---|---|---|---|---|
| N = | $14 \times 4 +$ | | | | $\dot{4}$ | = 60 | $4^3 \times 60$ | = 58·67 58·68 |
| | $14 \times 4 +$ | | 2 | | | = 58 | $2^3 \times 58$ | |

It will be seen on referring to the original Table that one of the *a-b-c-d* values was irregular with respect to a preceding one, but by this change it becomes quite regular. The dots over the 4 *indicate* that this figure as a whole is not to be cubed, but that it has to be taken as made up of four units, thus: $1^3+1^3+1^3+1^3=4$, *as in some other cases*—see original Table. The retention of the indices is for mathematical uniformity.

After introducing this amendment and comparing all my values of the Table with all those now published by Aston, it will be seen that there are 21 whole-number values in exact agreement with experiment and two departures from experiment by one unit only in each case; namely, Li 6 and B 10. Introducing the extreme values for magnesium by Dempster (see *Science*, December 10, 1920), which are 24 and 26, raises the agreement figure to 23.

Referring to the above departures, it will be noted that they are *even* numbers, whereas the valencies are *odd*. The valency rule thus seems to break down, but it is a curious fact that except for these two exceptions practically all the other isotopes of the Table are in accordance with the rule. Cobalt appears to have valencies of 2 and 3. Its calculated isotopes are 57 and 59—see Table. Nitrogen, though not isotopic, is a notorious exception to the rule, but this element is exceptional in other respects.

I have tried to account for the nitrogen irregularity by regarding N as truly bi- and quadrivalent, and by assuming that ammonia, for example, was a mixture of isotopic *molecules* $NH_2$ and $NH_4$ in equal proportions, the mean being apparently $NH_3$; but, needless to say, this scheme did not seem justified from the study of various experimental data. There are no doubt surprises in store in connection with these matters which may turn out to be as startling as the breaking up of the nitrogen atom by Rutherford.

## UNIVALENT OXYGEN. PREPARATION AND OXIDATION OF MESITOL.

By C. W. PORTER and F. H. THURBER.

WHEN Gomberg isolated triophenyl-methyl and produced evidence that other radicals are capable of independent existence (Gomberg, *Ber.*, 1902, xxxv., 3915), he revived the hopes expressed by Dumas, Kolbe and Frankland, and gave a new

impetus to research in organic chemistry. At the present time several compounds of trivalent carbon are known; but with the exception of Kohler's triphenyl-indyl (Kohler, *Am. Chem. J.*, 1908, xl., 217) they all belong to the triarylmethyl class. The search for new types of radicals, and especially those representing unsaturated conditions in elements other than carbon, has not been very successful, except in the discovery of compounds of divalent nitrogen derived from hydrazine and carbazole. Wieland found that tetra-anisyl hydrazine in benzene has an abnormally low molecular weight; develops a colour which deviates from Beer's dilution law; and forms an addition product with nitric oxide. One or two other substituted hydrazines displayed similar properties (Wieland, *Ber.*, 1912, xlv., 2601). Branch and Smith obtained a derivative of carbazole which dissociates into radicals of divalent nitrogen (Branch and Smith, *Jour. Am. Chem. Soc.*, 1920, xlii., 2405).

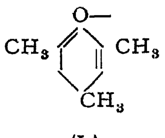
Porter and Borgstrom prepared tetraphenyl-diarsine (Porter and Borgstrom, *ibid.*, 1919, xli., 2048) and corresponding derivatives of phosphorus and although these products absorbed oxygen from the air and exhibited other evidences of unsaturation, their properties could be accounted for without assuming any measurable dissociation. A lead compound bis (lead triphenyl), $(C_6H_5)_3Pb\text{-}Pb(C_6H_5)_3$, acquires a colour when heated, but gives no other evidence of change in structure, and the corresponding derivative of silicon does not dissociate at all (Schlenk, *Ber.*, 1909, xliv., 1179).

An attempt to isolate an oxygen radical was made by Pummerer (Pummerer, *ibid.*, 1914, xlvii., 1472; Pummerer and Cherbuliez, *ibid.*, 1914, xlvii., 2957), who oxidised several naphthol derivatives with potassium ferricyanide and other reagents, thus obtaining tautomeric products corresponding in composition to the original naphthols (or to the peroxides derived from them). Some of these bodies gave coloured solutions deviating from Beer's law; and the molecular weights were lower than the calculated values for peroxides. The many possible intramolecular rearrangements, however, made uncertain any deductions with respect to the structures of these oxidation products.

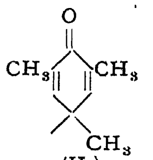
Hunter and Woollett have expressed the opinion (Hunter and Woollett, *Jour. Am. Chem. Soc.*, 1921, xliii., 142) that the complex amorphous oxides which they obtained from trihalogenated phenol salts are condensation products of residues containing univalent oxygen; and that in the process of building up these massive structures some of the oxygen valences remain free.

In our work, which has been in progress during the past two years, the aim has been to eliminate some of the possibilities for intramolecular rearrangements, and particularly the shift of a group from phenol oxygen to an *ortho-* or *para-* carbon; to accomplish this we worked with a simple phenol, mesitol, (2,4,6-trimethylphenol), in which the positions *ortho* and *para* to the hydroxyl are occupied by methyl groups.

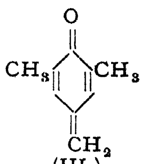
The compound was oxidised by silver oxide and from a mixture of oxidation products we obtained a red crystalline compound melting at 224° to 226°. It has the composition of the peroxide we hoped to obtain; its reactions, however, indicate that it is a quinhydrone. The following formulas represent possible structures of the primary oxidation product.



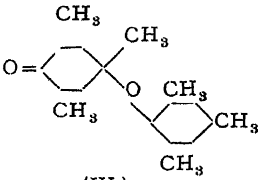
(I.)



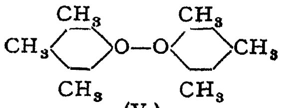
(II )



(III.)

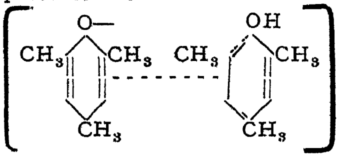


(IV.)

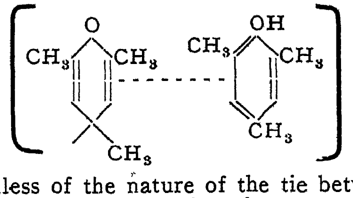


(V.)

Formulas I., II , and III. are excluded, for the molecular weight of the product is above 225, whereas these formulas represent compounds having the molecular weight 135. Moreover, the quantity of any reducing agent required to discharge the red colour of a solution of the compound is only half the amount theoretically necessary to reduce I. or II., and only one-fourth the amount required for Formula III. Formulas IV. and V. are also unsatisfactory, for, although they are in fair agreement with the determined molecular weight, their complete reduction would require the same quantity of reducing agent per grm. of substance as required by Formula I. or II. We believe the red crystals represent a quinhydrone composed of equimolecular quantities of unoxidised mesitol, and an oxidation product corresponding to Formula I. or II. The nature of the union between the two nuclei is unknown, but may be similar to that existing between quinone and hydroquinone in the ordinary quinhydrone formed when hydroquinone is oxidised. Until further evidence is secured, its structure may be represented as :—



or

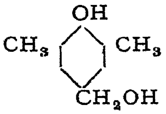


Regardless of the nature of the tie between the two nuclei, it is evident that the compound containes an odd or unpaired electron—the outstanding characteristic of a free radical (Lewis, *Jour Am. Chem. Soc.*, 1916, xxxviii., 770)—for it is re-

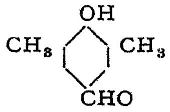
duced by the addition of only one hydrogen atom per mol of the compound. It represents therefore an addition to the very limited number of known types of odd molecules. Several years ago, G. N. Lewis suggested that such compounds should be capable of independent existence. To quote his words: "If proper protection against intramolecular rearrangement be provided, we may predict that di-aryl substituted hydrogen peroxide will be prepared, which in turn will dissociate into mono-aryl oxide, ArO, the odd molecule, or free radical, of univalent oxygen" (Lewis, *Proc. Nat. Acad. Sci.*, 1916, ii., 586).

Our oxidation product crystallizes in fine red needles and in benzene forms a deep red coloured solution containing less than 0·1 per cent of the solute. It is even less soluble in alcohol, and insoluble in water. It is rapidly reduced to colourless products by an alcoholic solution of potassium or sodium hydroxide, but is fairly stable in a very dilute acid solution of alcohol. Stannos chloride, titanous chloride, and ferrous sulphate rapidly discharge the colour of an alcohol solution of the compound, the original colour being restored by treatment with silver oxide. The quantity of any reducing agent required to discharge the colour corresponds to the calculated value for the quinhydrone formula or half the quantity required for Formulas I., II., IV., or V. The crystals dissolve in concentrated sulphuric acid, giving a very deep red solution, the colour of which is discharged by diluting with water. Nitric acid converts it at once into colourless products. These colourless products we have not yet identified.

The red compound is totally unlike the oxidation products of mesitol obtained by Bamberger (Bamberger, *Ber.*, 1903, xxxvi., 2030) and Thiele (Thiele and Eichwede, *Ann.*, 1900, cccxi., 366). Bamberger used Caro's acid, and Thiele employed amyl nitrite as the oxidising agent. The formulas assigned to their products are:—



and



Both are colourless and water-soluble.

The calculated molecular weight for the quinhydrone is 271. The values we obtained were between 225 and 250. On account of its slight solubility we could not get a freezing-point depression equal to 0·01°, and we do not consider the molecular weight determinations sufficiently accurate to justify the conclusion that the low values are due to dissociation. On the other hand, the measurements are good enough to indicate that undissociated molecules contain two mesitol residues.

## *Experimental.*

*Preparation of Mesitol.*—Mesidene (2,4,6-trimethylaniline) was made from 1,2,4,-xylidine and methyl iodide by an application of the Hoffman rearrangement. The success of the method depends upon the purity of the reagents, control of the temperature, and the time of heating. Pure 1,2,4-xylidene was obtained from the mixed isomers (commercial product) by precipitation of the acetate with glacial acetic acid. The crystals were pressed, washed with acetic acid, and dried. The free xylidine was liberated from the crystals by means of sodium hydroxide solution, separated from the water layer and distilled.

Equimolecular quantities of 1,2,4-xylidine and pure methyl iodide were poured into Pyrex bomb tubes packed in ice. After standing for two or three hours, the tubes, now containing the viscuous amber-coloured quaternary ammonium compound, were sealed, heated during the course of an hour to 260°, and held at that temperature for three hours. (The optimum temperature for the rearrangement seems to be 260°. At temperatures much lower the change does not occur, and at higher temperatures there is considerable charring. We used an electric autoclave with a thermoregulator, and maintained a temperature that did not vary more than 3° or 4°.) The red, waxy, or semi-crystalline product was transferred to a flask and neutralised with sodium hydroxide solution. The oily layer, mesidine, was separated and distilled under reduced pressure.

*Mesitol.*—The mesidine was diazotised in the presence of an excess of dilute hydrochloric acid solution and warmed. Mesitol separated as a red oil. It was removed from the water layer, dried with sodium sulphate, and distilled under 10 cm. pressure. On standing the distillate crystallised. Recrystallisation from 20 per cent alcohol gave pure white feathery crystals melting at 69°.

*Oxidation of Mesitol.*—Flasks containing 25 g. of moist silver oxide, 5 g. of mesitol, and 500 cc. of benzene, were sealed and shaken in a thermostat at 50° for four hours.

Each solution acquired a deep red colour, and a fine red crystalline compound precipitated. On evaporation the filtered solution yielded a small quantity of the red compound, but the major portion was obtained by elutriation from the residual mixture of silver oxide and the red compound remaining in the flask. The crystals are much lighter than the other components of the residue, and can be washed out with benzene. The substance is insoluble in water, and only slightly soluble in alcohol, chloroform, and ether. It melts at 224—226°.

### *Analyses.*

| Subs. G. | $H_2O$ G. | $CO_2$ G. | H. Per cent. | C. Per cent. |
|---|---|---|---|---|
| 0·1050 | 0·0756 | 0·3113 | 8·00 | 80·80 |
| 0·1200 | 0·0853 | 0·3520 | 7·90 | 80·00 |
| 0·1425 | 0·1045 | 0·4206 | 8·15 | 80·50 |

Calculated for quinhydrone: 8·48, 80·81.

### *Molecular Weight.*

Cryoscopic method. Solvent, Benzene, K=50.

| Subs. G. | Solvent. G. | Temp. °C. | Mol. Wt. |
|---|---|---|---|
| 0·0322 | 109 | 0·007 | 230 |
| 0·0270 | 100 | 0·006 | 225 |
| 0·0900 | 239 | 0·008 | 245 |

Calculated for quinhydrone: 271

*Reduction with Hydrazine* (Hunter and Woollett, *Journ. Am. Chem. Soc.*, 1921, xliii., 138).

| Subs. G. | Vol. $N_2$. Cc. | Temp. °C. | Barom. Mm. | Wt. $N_2$ liberated by 271 G. substance. |
|---|---|---|---|---|
| 0·1105 | 2·7 | 15 | 760 | 7·72 |
| 0·1240 | [illegible] | 20 | 758 | 7·68 |
| 0·1000 | 2·2 | 15 | 760 | 6·95 |

Calculated for quinhydrone: 7·00

*Reduction with $SnCl_2$*

$SnCl_2$ in dilute HCl standardised by titration with $KMnO_4$ solution containing 0·5000 g. of $KMnO_4$ per litre.

10·00 cc. of $SnCl_2$ =O= 15·60 cc. of $KMnO_4$. Subs., 0·03, in 80 per cent alcohol reduced by 4·6 cc. of $SnCl_2$ solution. Equivalents of reducing agent required for 271 g. of substance = 1·02. Calculated for quinhydrone: 1·00.

*Reduction with $FeSO_4$.*

$FeSO_4$ in dilute $H_2SO_4$ standardised by titration with $KMnO_4$ (0·5000 g. per litre). 9·70 cc. of $FeSO_4$ =O= 17·05 cc. of $KMnO_4$. Subs., 0·052 in 80 per cent alcohol reduced by 7·10 cc. of $FeSO_4$. Equivalents of reducing agent required for 271 g. of substance = 1·03. Calculated for quinhydrone: 1·00.

*Summary.*

Mesitol in benzene solution at 50° is oxidised to a red crystalline compound which is unsaturated and is readily reduced to colourless products.

Its molecular weight indicates that it contains two mesitol nucle.

Its reduction is accomplished by half the quantity of reducing agent that would be required if all the oxygen were quinone or peroxide oxygen

It is reduced to a saturated product by addition of an uneven number of hydrogen atoms or other electro-chemical equivalents, indicating that it has an impaired or odd electron.

The properties of the compound are accounted for on the basis of a formula containing an oxidised mesitol residue possessing either univalent oxygen or trivalent carbon more or less firmly held by an unoxidised molecule of the phenol.—*Journal of the American Chemical Society*, May, 1921.

## FUEL PROBLEMS OF THE FUTURE.*

By Sir GEORGE T. BEILBY, F.R.S.

CIVILISATION on its physical side is based on fuel. Of all the powers of Nature which have been turned to his use and convenience by man, "Fire" stands out with a distinction which is unique. The kindling of the first fire of dried leaves and branches by our prehistoric ancestors marked the beginning of the transfer of this mighty power from the gods to man; and new possibilities of prodigious import were opened up. With fire at his command, a new dividing line was established between man and the lower animals, and a higher and more social standard of living became possible. The horrors and dangers of the darkness of night were greatly mitigated, social instincts were aroused through the nightly gathering round this new source of light and warmth, while imagination and thought were stimulated. The charred stick supplied the budding artist with his first pencil; while the glowing embers were the laboratory furnace in which the coming chemists and metallurgists made their first observations on the effects of heat on rocks and stones.

Fire—first automatically and then deliberately—became the test to which all materials were submitted. The arts of the craftsman were based on these observations; the smelting of metals, the bending of wood, the singeing of skins, the melting of gums, and the boiling of water, started a whole train of new possibilities—each step in discovery opening the way to new adventures. It is no exaggeration to say that the practice of observation and experiment on which the physical science of to-day is founded had their origin in the first fire kindled by man.

In the management of the wood fire the first lessons in the properties of fuel were learned. The flaming stage, followed by the steady and more concentrated heat of the glowing embers, naturally led to the collection of more massive embers by the control of the earlier stages of combustion—thus leading up to charcoal burning, by which the worker in metals was supplied with an ideal fuel for his operations. Thus the carbonisation of raw fuel as a means of raising the availability of the potential therms it contains, had its origin in the remote past.

It is far from our present purpose to follow through the ages the romantic history of the association of fuel with civilisation. Enough has been said to justify my opening remark that civilisation on its phsical side is based on fuel. This interrelation has developed new features during and since the war; and the future production and use of fuel in this country has become closely associated with social ideals which involve the raising of the standard of living among the mining class. This, indeed, is the most pressing of the fuel problems of the near future. Can coal again be produced at a price which will enable this country to take its place in the markets of the world, while the present standards of wages and working hours are maintained? Careful and impartial students of the economic facts of the situation tell us that this is not possible. Merely to regain an entrance into the iron and steel markets of the world, we are assured that the coal used in this industry must not cost more than 18s. to 20s. per ton. For the great transport services of the country, a slightly higher cost for coal might be faced if all the available measures of economy in its use as fuel are adopted. It is obvious that, without a greatly increased output per man, the earnings of the miner cannot be maintained at their present figure.

This end can only be attained by genuine co-operation between the coalowners and the miners; any half-heartedness on either side will in the long run lead to failure. How is such co-operation to be secured? The miners have pinned their faith to nationalisation as supplying the solution of the problem. The nationalisation which the more extreme section have in view appears to involve the handing over of the direction and control of the industry to nominees of their own, who would in effect be pledged to regard the wage-earners' interests as paramount.

While the nation is in sympathy with the raising of the standard of living of the miners, and the improvement of working conditions in the mines, it has no belief that nationalisation would supply a commonsense and practical solution of the problem. The nation also realises that no system of bureaucratic control would adequately replace the individual and collective effort which is necessary for the development of this complicated industry.

The significance of the patience and self-sacrifice of the consumers of coal right through

*Delivered in the theatre of the Institution of Civil Engineers, London. Inserted by favour of the *Gas Journal*, June 29, 1921.

the difficult times which culminated in the strike of the past months, appears to have been missed or misinterpreted by both miners and mineowners, and to some extent also by the Government. This remarkable patience on the part of the whole British public does not mean that they are either ignorant of, or indifferent to, the future availability and cost to them of the fuel on which their daily lives must depend both directly and indirectly. If a permanently higher cost of fuel must be faced, then its availability must be correspondingly increased.

To take only one aspect of this question of "availability" which affects every consumer, from the highest to the lowest—the quality of the coal as it is raised to the surface and distributed by rail and road—this is a matter which at present is entirely in the hands of the mineowners and the miners. Every householder knows that the quality of the coal he or she receives has greatly deteriorated during and since the war. Stones and other inferior materials have been received and paid for as coal at the greatly enhanced prices of the day. The very fact that this burden is most widely felt by individuals renders it unsuitable for dealing with by statistics. For our present purpose, therefore, the experiences of the large consumers can be more usefully considered.

The gas undertakings of the United Kingdom are responsible for the distribution of the heat derived from about 20 million tons of coal per annum. This, in round numbers, is not less than one-eighth of the total amount of coal consumed in the country. The experiences of these undertakings as regards the depreciation in the quality of coal they have received during and since the war have been freely disclosed and discussed by their engineers and directors; and on the strength of these representations the Board of Trade agreed to sanction a very substantial reduction in the calorific value of the gas delivered and paid for at the old rates by the consumers. Even with this relaxation in quality, the gas undertakings found it difficult, and in some cases impossible, to maintain adequate supplies of gas to their consumers, while the coke in which the whole of the inert and valueless material in the coal was concentrated was rendered greatly inferior as a fuel.

During the inquiry of the Fuel Research Board into the question of gas standards, they were in close touch with this subject; and my present remarks are based on first-hand knowledge. As a result of our recommendations, the Board of Trade adopted the "therm" of 100,000 B.Th.U. as the future unit of charge to the consumer for the gas he receives; and I merely refer to the change at this stage in order to demonstrate the logical application of this principle to the question of the quality and price of coal. If the gas undertaking is in future to be paid only for the therms delivered to the customer, it is entitled to throw at least a portion of its responsibility on the coalowners and miners by paying only for the potential therms received in the coal, and not for inert and inferior materials which are not only valueless and detrimental to economical working in the retort-house, but lower the value of the coke produced.

Among other large consumers of coal, electricity generating stations occupy a very important place. Of the total cost per unit in the generation of electricity, the larger proportion is due to the fuel consumed. This cost has been trebled or even quadrupled since 1914—largely, no doubt, owing to the direct rise in the price of coal, but also to a substantial extent through the deterioration in quality of the coal supplied. By the kindness of Sir Alexander Kennedy and of Mr. Herbert Jones, the Electrical Engineer of the London & South-Western Railway, I am in possession of the working results of the first quarter at two important generating stations in London. These figures will be again referred to in another connection. For our present purpose, I will only draw attention to the coal experiences at these stations. In the case of the Central Electric Supply Company, the calorific value of the coal received for thirteen weeks averaged 10,582 B.Th.U., cost 45s. 2d. per ton, and its ash content was 18·4 per cent. The weekly ash figures ranged from 16·3 to 20·1 per cent. In the winter of 1914-15, the corresponding figures were: Calorific value, 10,800 B.Th.U.; cost per ton, 14s. 6d.; ash content, 13 per cent. The ash excess on the coal supply during the present year was therefore 5·4 per cent, or rather more than 1cwt. per ton.

At the Durnsford Road power house of the London & South-Western Railway at Wimbledon, the average calorific value of the coal received was 10,900 B.Th.U., and the ash content 16 per cent.

Examples of this kind could be multiplied indefinitely from the experiences of private firms and public institutions. But the foregoing are sufficient to establish my point, which is that in view of the stage reached by the national coal problem, the time has come when the vital interests of the consumers must be reckoned with in any settlement that is arrived at. These interests require that the mineowners and miners must alike realise that their responsibility is not met by the output of mere material at the pit head and its distribution to consumers by road or rail. Whether this material is to be consumed in its raw state as fuel, or whether it is to be converted into fuels of higher availability by gasworks or other carbonising and gasifying agencies, what counts is its thermal value. To the miner it may seem a revolutionary proposal that he should be paid by the therms he sends to the surface; but as he himself possesses views in connection with the development of his industry involving a treatment of the national fuel problem from an entirely new and revolutionary point of view, he cannot logically ignore the effects on the consumer and on the nation at large of the permanently increased cost of fuel which must result if his claims for a higher standard of living are to be realised.

To my mind it would be a serious set-back to our civilisation if the only solution of the economic problem involves the production of coal at prices which are insufficient to ensure for the miner a steady amelioration of the conditions under which he lives and brings up his family; and I for one would be prepared with good heart to face the working out of the more efficient use of fuel which is absolutely necessary if a higher price is to paid for coal. This, however, would only be on one condition—that there is genuine co-operation of coalowners and miners, not only in the organisation of output on modern lines, but

in the endeavour so to sort out and prepare the output by screening and washing the coal at the pit-head that the consumer is only called upon to pay carriage on the actual fuel value received. The gas or electric undertakings are certainly entitled to press home to the miner the fact that, as the consumers of gas and electricity only pay them for "therms" or "units" received, they in turn should pay the coalowners and miners on the same basis, though at a cost per therm which will leave a reasonable margin of profit on their operations.

Probably the iron and steel industry will be most severely handicapped by any permanent increase in the price of coal, as fuel enters into its operations to so large an extent. The opinion has been expressed by experts in this industry that, though a reduction to 18s. or 20s. per ton in the price of coal suitable for the making of iron and steel might enable the industry to recommence, it is doubtful whether it coulld ultimately hold its own in the markets of the world. To ensure this, it is considered that it would be necessary for coal to return to the neighbourhood of its pre-war price. It has been suggested (Coal Conservation Committee, Ministry of Reconstruction, 1918, pp. 77-81) that a considerable saving of fuel might be effected by so grouping the elements engaged in the production of finished steel—coke ovens, blast furnaces, gas producers, steel furnaces, and rolling mills—that the heat from all sources could be pooled at a common centre of heat and power. By this means it was considered that any excess of heat available at one stage might be made available at other stages in which an excessive demand existed. In this way it was believed that the consumption of coal per ton of finished steel might be reduced to 35cwt. per ton. If an ordinary figure of consumption of 45cwt. be taken, then a saving of 10cwt. of coal per ton of steel might result from grouping. With coal at 18s. per ton the saving would amount to 9s. per ton of steel. But this estimate takes no account of the large capital which would have to be sunk in scrapping and replacing existing works.

The future of British iron and steel production is obviously so closely associated with the future price of coal, that no outsider is in a position to solve the problem. We can say, however, that substantial fuel economies are possible, though the extent to which this would justify a higher price for coal is still quite uncertain.

Before considering in technical detail some of the fuel problems which are more immediately before us, it may be well to pass in review the fuel position of the world, as it is disclosed by the most recent figures of production. For our present purposes our survey must be on broad and simple lines, which will enable us to grasp the whole question in due proporiton and in its true perspective. Proportion and perspective, as the exponents of the doctrine of relativity might remind us, depend entirely on the point of view of the observer. The facts and figures of the fuel resources of the world are the common property of the experts of all civilised nations. They may be regarded as being like the immutable laws of Nature; but the proportion and perspective in which these facts and figures range themselves are different for the observers and commentators of each of these nations. In our own survey, we shall be wise to have in our minds some recognition of these widely different points of view

In Great Britain, as a maritime nation, we cannot, either on political or commercial grounds, ignore the points of view of other nations inside or outside the circle of the Empire.

An interesting review of the world's coal supply in 1920 is given in the United States Geological Survey. The total output, including brown coal and lignite, amounted to 1300 million metric tons. This is within 3 per cent of the maximum output which was reached in 1913 and 1918. Of this total output—

| | Per cent. |
|---|---|
| The United States of America produced... | 45 |
| Great Britain and the British Empire produced ... | 22 |
| Germany produced ... | 19 |
| Other countries, ranging from 2½ per cent downwards, produced ... | 14 |
| | 100 |

One of the most significant features revealed by this survey is the remarkably rapid development in the winning and use of brown coal and lignite in Europe and particularly Germany. The output in Germany in 1919 had reached the huge figure of 93·8 million tons; but this was overtopped in 1920 by an output of 111·6 million tons—an increase in one year of nearly 18 million tons. The total European output in 1920 amounted to 140·7 million tons, made up as follows:

| | Million tons. |
|---|---|
| Germany ... | 111·6 |
| Czecho-Slovakia ... | 19·7 |
| Jugo-Slovakia ... | 2·5 |
| Austria ... | 2·5 |
| Italy ... | 1·6 |
| Netherlands ... | 1·4 |
| France ... | 1·0 |
| Spain ... | 0·5 |

The output of ordinary coal in Germany for 1920 was 140·8 million tons. The brown coal industry in that country is of old standing; and its rapid development in recent years is based on sound knowledge and experience. Though in its natural state a less concentrated fuel than bituminous or anthracite coal, brown coal has many points in its favour. The chief of these is the low cost at which it can be won as compared with ordinary coal. Where extensive deposits of great thickness occur, these can be worked opencast, and excavated by machinery. The winning of brown coal is thus on an altogether different basis from coal mining, with its deep and costly underground roads and workings, which involve heavy costs for timbering, pumping, and ventilation. The manual labour required is much smaller in amount for a given output, and is of less highly specialised type; while the special dangers and uncertainties of coal mining are practically absent. The capital charges being mainly on surface roads and on excavating machinery—are relatively light, as compared with the heavy initial and permanent charges involved in the sinking and equipment of shafts or mines. Brown coal, though it contains from 40 to 60 per cent of water, is to-day by far the cheapest source of thermal units. Its further manufacture by drying, briquetting, and carbonisation, can be carried out close to the point

of excavation, and under conditions favourable to production on a large scale, and therefore at a low cost.

The glowing accounts of this development which have appeared in the technical Press during the past two years may have struck us as exaggerated; but the solid fact remains that the output of lignite in Germany last year was 111 million tons. Germany has already faced the fuel problem of the future so far as she herself is concerned.

In view of the hard facts and figures which are now before us, it is not surprising that Germany's example is being followed, not only in Central Europe, but in Victoria and in Canada. In Victoria, extensive deposits of brown coal exist in Central Gippsland, which are estimated by Mr. H. Herman, the Director of Geological Survey, to contain 30,000 million tons. The main deposits near Morwell are hundreds of feet in thickness, and lend themselves admirably to opencast working on an enormous scale. Considerable progress has already been made in the development of these deposits; and since the commencement of operations in 1916, 400,000 tons of brown coal have been mined and sold. When the excavating methods become more perfectly organised, it is anticipated that the coal will be produced at the mines at 2s. 3d. per ton. It contains from 40 to 50 per cent of water; so that in heat value two tons is equal to about one ton of ordinary coal. A 50,000 kilowatt generating station is being installed at Morwell for the transmission of current to Melbourne. Though a considerable market appears to exist for the coal as it is mined, it is intended to establish briquetting and carbonising plant at the mines; so that fuels of higher availability will be produced from the raw coal. In 1920, a sample of this coal was received here, and experiments on its carbonisation were carried out at the Fuel Research Station.

In the Dominion of Canada, experiments are in progress on the briquetting and carbonisation of the brown coals of Manitoba and Saskatchewan. These experiments are being carried out under the auspices of the Dominion Government and of the Government of the Province of Saskatchewan.

Somewhat allied to the lignite problem is that of the development of peat as a fuel. The Dominion Government of Canada is keenly interested in this question; and I shall have something more to say on the subject at a later stage Germany also is preparing for important developments, some of which are described in the *Engineer* for April 22, 1921. The Wiesmoor plant, which has been in use since 1910, is now regarded as obsolete; but during the ten years it has been in use, much valuable experience has been gained in the winning and use of peat. The average fuel consumption is stated to be from 2·7 to 3 kilos. of partially dried peat sods per k.w. hour, and the cost of the peat is taken at 5 marks per ton. It is now proposed to establish a line of generating stations fired by peat extending from Königsberg in the east to Wiesmoor in the west.

The world's output of brown coal and lignite in 1920 was about 143 million tons, or 11 per cent of the total coal output of 1300 million tons. From the European point of view, the significance of this fact must not be gauged in terms of this moderate percentage. According to the extent to which Germany can meet her own requirements for heat and power by the development of lignite, peat, and water power, the output of her coal mines will be set free for export, and she will thus take a more important place in the markets of the world. The coalowners and miners of this country would be well advised to keep an eye on the development of brown coal and lignite in Germany and elsewhere.

(To be continued)

## UNIVERSITIES, RESEARCH, AND BRAIN WASTE *

By J. C. FIELDS, Ph.D , F.R.S.

(Concluded from p. 77)

THE waste of brain in this world is a tragedy of the first order. There is none greater. This was brought home to us with peculiar emphasis during the war. When Moseley was killed at Gallipoli scientists everywhere felt a sharp pang. Here was a young man who had crossed the threshold. He had just had time to prove his genius. Almost at his first attempt he left his imprint on the science of physics, and great things were expected of him. His sudden cutting off did a great violence to the sense of the fitness of things in the minds of those who knew what a loss it meant to science. The toll of Trinity College, Cambridge, in the war was in the neighbourhood of 2,000. Of these, some had already been productive, and others gave great promise. The most gifted of our young men went overseas, and many of them will never return. Among the latter were two of gold medallist standing in my own Department. The sacrifice of a young man of exceptional ability seems to accentuate the unreason and injustice of warfare. Why should he not have been permitted to fulfil his natural destiny, to lead an intellectually productive life, and perhaps add a permanent increment to the heritage of the race? Yet the same sacrifice of exceptional gifts, the same waste of brain power, is going on regularly in our midst in peace times and we pay no attention to it. What is possible in this regard I have illustrated by the history of mathematics in America. Successive generations of potential mathematicians were wiped out. They never knew what struck them. Their contemporaries never knew that nature intended them to be mathematicians. The story of the Dockyard Schools is full of suggestion as to the waste that must be going on. We pause to think when we hear of a man like George Green, who was discovered at 40, graduated at Cambridge at 44, and died at 48, after leaving his permanent mark on the history of mathematics and physics. It is said that his later years were saddened by the realisation of the fact that the greater part of his life had been wasted. How many George Greens are there who die before 40? How many who are not discovered before 48?

There is one general formula which will enable us to avoid all waste of brain, but we should endeavour in every possible way to salvage all we can. It would, no doubt, be helpful to have the advantages of a university or higher technical education presented from different view-points to

*Reprinted from the *Transactions of the Royal Canadian Institute* February 1921.

the pupils in the secondary schools, preferably by visiting lecturers. Their studies, too, should include something of a biographical or narrative character touching on the lives and work of the great scientists. This might even with advantage be introduced into the elementary schools. Matter could readily be selected which would not be lacking in romance.

Some adequate reference it seems to me should be made to science in the teaching of history in the schools. Modern history, as I understand it, is an account of how a people, starting out under certain conditions at a given time in the past, have arrived at where they now find themselves. The most important agent involved in the transition, the largest factor by far concerned in modifying the conditions of living during the past two centuries, has been science. Is it not of the first importance that every boy and girl should be made aware of this fact?

By stimulating the interest of the pupils of the preparatory schools in science, by visualising university opportunities and by establishing a system of scholarships such as we have already referred to, we could doubtless increase considerably the number of students of ability in our universities. Those who do not go to the university, but leave the elementary or secondary school to earn their living, would at least carry away with them a certain respect for science and a recognition of the fact that the university has a useful function to perform in the life of the community. This would later on have its effect in helping to create a public opinion which would react more favourably to proposals for financial aid to universities and science.

A university should be sufficiently staffed to care for the needs of its students. Our own University is undermanned. The tutorial classes should be smaller. This is no good reason, however, why the members of the staff should be overworked. Junior instructors, who have research inclinations, should be given a chance to show the mettle that is in them. The more mature men, who have already proved themselves, should be given time for research. Only yesterday I was talking to a member of the staff who told me that for three weeks past he had been working till three in the morning and that for seven days in the week. The man in question is a research worker, but the work referred to had nothing to do with research This is, of course, exceptional, and it will not ordinarily be necessary for my colleague to work so strenuously. Even so it is a little inconvenient. The same man, too, worked till midnight daily during the last month of the vacation getting the materials required in his laboratory in readiness for the opening of the term. I asked him whether he received any pay for work overtime. His reply was an incredulous smile which, interpreted, meant how could any member of a university staff be so ingenuous as to ask such a question.

The case I have cited is an extreme one to be sure. There are plenty of members of the univrsity staff, however, who have more than enough to do, and there is none who has not enough to keep him busy. Of this the layman can rest assured. Further staff, of course, would mean more expense, but the Province would be well paid for its extra outlay.

There should be a larger number of places for research men in Canada. There should be more positions for them in the universities and more in the industries outside. The University of Toronto has begun to develop along research lines, and in the course of time, no doubt, much good Canadian brain-power will be salvaged which would otherwise go to waste. The projected Institute for Research at Ottawa will absorb some of the men trained by the University for research. It is to be hoped that the demand from the industries will grow. It might be well also to have such men in charge of the science departments in the high schools, and to encourage their research inclinations by furnishing them with adequate laboratory equipment. Something of this sort, I understand, it is proposed to do in England. (A provision in the Education Act enables local authorities to meet the cost of research work of educational value conducted by teachers in the schools.) This would all tend to conserve Canadian brain for Canada, and would check the leakage to the United States and other countries. Of the 15,000 living graduates of the University of Toronto, 1,700 are located in the Republic to the south of us. Between 400 and 500 others are domiciled abroad. McGill's loss to the United States is 1,500 out of 6,700 graduates.

It has been suggested that research professors and research associate professors be appointed in the departments of natural science of the University of Toronto, their duties to consist primarily in the prosecution of research on their own account, and in the training of young men of selected ability for research. The aggregate of these research men would be known as the research staff in natural science of the University of Toronto.

To me it appears that the organisation of such a group would, in addition to creating greater effectiveness within the university, have a two-fold benefit without. On the one hand, it would remind the laymen that there exists a body of men in the world whose business it is to advance knowledge, and on the other hand it would impress on them the fact that the University is not an institution whose sole function is to purvey knowledge, but that it has also another and quite as important function, namely, to add to knowledge and to train young men in order that they may add to knowledge in their turn.

The war has been wasteful of brain power. It has, however, taught us its value. In the work of reconstruction nothing can be of more importance than conserving and realising on the brain power of the nation. In this work the universities must play the leading role. If in our reconstructed country we shall have reduced brain waste to a minimum and increased brain output to a maximum, we shall have raised the greatest of all memorials to our boys who sacrificed themselves in France and Flanders in order that Canada should be saved from determination by Germany. It is for the Canada whose destinies will be determined by Canadians that they fought and died, and the Canada that is to be will be their monument. Let us make the monument a great and noble one. May it be worthy of those whom it commemorates.

## GERMAN COMPETITION.

THE "Report on the Economical and Financial Situation of Egypt," published by the Department of Overseas Trade (H.M. Stationery Office, Imperial House, Kingsway, W.C.2), contains much information that might be studied with profit by British manufacturers, particularly in reference to foreign competition and the requirements of Egypt. From a mass of important notes we select the following statement, which speaks for itself.

"German stationery is being sold at many Italian and Greek shops at very low prices, and the material appears to be of a good class. For five sheets of notepaper and five envelopes only 5 milliemes or 1¼d. is charged.

German glassware and chinaware imports increased very greatly during the latter months of 1920; cutlery of a cheap order is also being imported in large quantities, as well as table services of every kind and design. The majority of the teaspoons, sugar-tongs, and other small accessories of the table are, however, of a very glaring and vulgar order. Silver-gilt birthday spoons are selling at P.T.125 a dozen, sugar-tongs at P.T.65 each, and nickel-plated plates at P.T.30 each. Razors are sold at an average price of P.T.55 each, which cannot be called remarkably cheap.

German drugs are returning to the Egyptian market in large quantities, including the original saccharine tablets, Messrs. Bayer's aspirin, and "Odol," manufactured by their original producers. Saccharin and aspirin are being advertised in all the local papers; the latter is sold in bottles containing 24 five-grain tablets (standard English weight).

German dyes, *e.g.*, synthetic indigo and other coal-tar dyes, are also returning to this market in large quantities, the quantity being more than double, and the value nearly treble, that of imports from the United Kingdom.

Among recent patents taken out will be observed (1) the name of J. A. Reidel, Aktiensgesellschaft Chemical Manufacturers of Britz, 1-38, Reidelstrasse, Berlin, viz., the word "IDRAG" printed, written, or stamped, in any size, manner, shape, or form; and any letters black, white, or red, used in respect of their chemical, medicinal, photorgaphic and lithographic products; also the word "GENOSAN" as above in respect of their medicinal products; dated 12/1/21: (2) Badische Anilin & Soda Fabrik of Ludwigshafen; specification of invention having for title "Préparation stable à base d'indigo blanc"; dated 10/1/21.

German pianos, mouth-organs, and other musical instruments are being freely advertised in Egypt, the prices for mouth-organs being very low indeed. The exporter of the latter is Albert Wordlish, of Stettin, who is sending in addition large quantities of cigar-holders, pipes, &c., to Egypt, also at very low prices, owing to the low rate of exchange.

It is unfortunate that, owing to German firms being able to accept such very low prices, they have succeeded in wresting fairly large contracts from United Kingdom exporters for railway material required by the Egyptian State Railways, and other kinds of material and plant required by other Government Departments, *e.g.*, light railway permanent way for use in connection with oil workings by the Department of Mines on the Sinai Coast. Unless British steel firms are prepared to make a big sacrifice, in spite of prices at present ruling in Sheffield, and to guarantee within a specified period, in order to keep their hold on the market for Egyptian Government contracts, they must not be surprised to see all future orders secured by German, Austrian, or Belgian firms, particularly for railway material and rolling stock.

German (Bosche) dynamos have been arriving in great numbers and were quickly sold owing to the low price demanded, and also to the fact that either United Kingdom exporters had apparently overlooked the Egyptian market for some months, or had not delivered them in sufficient quantities for its needs, as British dynamos appear to be very scarce at present.

Quantities of German fittings and spare parts are returning to this market; also hand-spanners, wrenches, and other hand tools are being sold in most of the machinery shops. In this connection it is to be regretted that a British engineer spent five days recently trying to buy a Briggs T-head spanner, which he required for use at the Egyptian Government oil workings on the Sinai Coast, and, having finally failed to buy a single one, was compelled, owing to the urgency of the work required, to purchase a German article.

The products of Krupps, the A.E.G., and Borsig Wolf & Co., are sold by the Technical Supply Co. of Alexandria, a company formed for that purpose.

German bicycles of the "Ankard," "Eros," and "Oppeln" makes were imported in fair numbers during 1920, but their sale is not very extensive. The two first-named arrive as a rule without tyres, and are sold by agents at £E.10 a piece with tyres, and £E.6 without. The "Oppeln," with half-gallon petrol tank and motor on frame with springs, is sold at £E.35.

New German electric motorcars of the "Adler" make are arriving in good numbers, also without tyres, and are being sold at £E.120, being of the very small type. Mercedes and Daimler cars are being sold at prices ranging from £E.1,500 to £E.3,000.

It is interesting to note that nearly all the tyres fitted to these German motorcars and bicycles on arrival here are of British manufacture, and in the case of the "Eros" bicycle, a British-made tyre, 28×1½in., is the only one extant in this market which will fit it.

Nearly all the films shown in Egypt have hitherto been American or French productions, but of late many German films have appeared, and it must be admitted that they have proved of a very superior order. It is to be hoped that United Kingdom producers will make an effort to show their films in this country, where they would be sure to be appreciated.

## NOTICES OF BOOKS.

*Journal of Indian Industries and Labour.* Vol. I., Part 2. Printed at Calcutta by the Superintendent of Government Printing, India. (Can be obtained in London of the following Agents:—Messrs. Constable & Co., Kegan Paul, B. Quaritch, P. S. King & Sons, H. S,

King & Co., Grindlay & Co., Luzac & Co., W. Thacker & Co, T. Fisher Unwin, Wheldon & Wesley).

The second part of Vol. I. of this *Journal* contains much that is of interest. Sir Thomas Holland contributes an article on the principles which govern the grant of mineral concessions in India. His discussion of the grounds on which the mineral policy of a Government has to be determined explains the reasons for restrictions which are apt sometimes to appear unnecessarily irksome to those engaged in the development of the mineral resources of a country. The article concludes with a very useful summary of the rules for the grant of prospecting licences and mining leases which are at present in force in British India.

An interesting account of the Rajputana salt industry, with particular reference to the salt works on the Sambhar Lake, is given by Mr. P. C. Scott O'Connor, an officer of the Northern India Salt Revenue Department, who has studied the history of Government control over salt production and has had considerable personal experience of the actual work of producing salt for the market.

Mr. J. W. Meares, in an article entitled "The Hydro-Electric Survey of India," explains in a lucid manner the potentialities of India in the matter of sources of water power. He discusses the various methods by which water can be harnessed in order to produce power for the development of industries and the provision of public conveniences without interfering with its function of irrigation. An account is given of the origin of the hydro-electric survey of India, of its results up to date, and of the limits within which its work is confined. Mr. Meares' remarks on the proper utilisation of electricity will be of use to those who have to weigh the comparative advantages of this and other sources of power.

Mr. Clow contributes a thoughtful article on the subject of "Factory Children and Education." The history of legislation relating to the various restrictions on the employment of children in factories is given and the comparative merits of the two schools of thought, one of which favours the prescription of educational tests before employment and the other the putting of compulsion on employers to provide education during the period of employment in a factory, provides an interesting contribution to the discussion of this difficult subject.

The subject of "The Hide, Skin, and Leather Trades and Boot and Shoe Manufacturing in India" is treated by Sir Henry Ledgard, who was until recently the Honorary Adviser to the Government of India on Boot Production. A detailed account is given of the methods introduced into the manufacture of boots for the Army in India during Sir Henry Ledgard's short term of office. The article concludes with a summary of the position of the leather and boot industries in India at the present time.

An interesting address on the subject of chemical research for the development of industries in India, which was read by Dr. E. R. Watson at the last meeting of the Indian Science Congress, is reproduced as an article in the *Journal*. Dr. Watson pays particular attention to the possibilities of producing in India the essential munitions of war which he claims should be the foremost consideration in the industrial policy of the country.

An outline of the present position of technical and industrial education in Bengal is the subject of a short article by Mr. W. H. Everett, which deals with education under the heads of civil engineering, surveying, mechanical and electrical engineering, mining, weaving, commercial education, and art.

Other items of interest are a summary of information regarding industrial disputes in India during the first quarter of the year, miscellaneous notes on various subjects, including the bleaching of shellac, the investigation of cotton stalks as a paper-making material, three short notes on subjects of industrial interest contributed by Sir Alfred Chatterton, and a statement showing the kind, quantity, and cost of stores purchased in India by Government during the three official years ending 1919-20. A new feature of the *Journal* is the publication of reviews of recent publications.

A notice announces that eight bulletins of Indian Industries and Labour have now been published, and seven more are in the press.

## CHEMICAL NOTICES FROM FOREIGN SOURCES

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. clxxiii., No. 3.

"The Distribution of Electrons in Heavy Atoms."—By MM. A. Danvillier and L. de Broglie.

"The Diffraction of X-rays by Liquids."—By M. A. Debierne.

"The Resistivity of the Monosulphide to Monoselenide of Thallium."—By M. H. Pélabon.

"The Magnetic Properties of the Metals of the Alkaline Earths in Combination."—By M. Paul Pascal.

"The Rôle of Gaseous Impurities in the Catalytic Oxidation of Ammonia Gas."—By M. Eugene Decavrière.

"The Preparation of Calcium Carbide by Calcium Ammonium and Acetylene."—By MM. L. Hackspill and E. Botolfsen.

"A New Reaction of Ammonia."—By M. Couat D. Zenghelis.

"A New Method of Preparing Sodium Derivatives of True Acetylenic Hydrocarbons."—By M. Picon.

"The Polymerisation of Glucosanes."—By MM. Amée and Jaques Pictet.

"The Nitro and Amido Derivatives of Methyl Ethyl Benzene."—By M. Alphonse Mailhe.

## NOTES.

Market for Chemicals in the Netherlands East Indies.—His Majesty's Commercial Agent in Batavia (Mr. H. A. N. Bluett), has forwarded to the Department of Overseas Trade the official returns of the import of chemicals into the Netherlands East Indies for the first two months of 1921. The chemicals named are alum, caustic soda, sodium carbonate, iron sulphate, calcium carbide, and copper sulphate. Except in the case of the

last two, the returns show a very considerable falling-off in trade with Great Britain in 1921 as compared with that of 1920, with a corresponding increase on the part of Germany. Further particulars can be obtained by application to the Department of Overseas Trade, 35, Old Queen Street, Westminster, S.W.1.

PRODUCTION AND INDUSTRY (IRON AND STEEL) — The production of iron and steel, which in 1920 almost approximated the 1913 figures, shows a large decline in the first six months of 1921, the actual figures, together with the corresponding figures for 1920, being as follows:—

| | Pig Iron. | | Steel Ingots and Castings. | |
|---|---|---|---|---|
| | 1920. Tons. | 1921. Tons. | 1920. Tons. | 1921. Tons. |
| January | 665,000 | 642,100 | 754,000 | 493,400 |
| February | 645,000 | 463,600 | 798,000 | 483,500 |
| March | 699,000 | 385,500 | 840,000 | 357,600 |
| April | 671,000 | 60,300 | 794,000 | 70,600 |
| May | 739,000 | 13,600 | 846,000 | 5,600 |
| June | 726,000 | 800 | 845,000 | 1,900* |
| Total | 4,145,000 | 1,565,900 | 4,877,000 | 1,412,600 |

* This refers to castings only.

It will be seen that a considerable decline took place before the beginning of the coal dispute, but the decline in the United States was equally serious, and no improvement in output in that country is yet visible:—

| U.S. Output of | Pig Iron. | Steel. |
|---|---|---|
| 1920 Monthly average ... | 3,077,000 | 3,392,000 |
| 1921 April ... .. ... ... | 1,193,000 | 1,441,600 |
| 1921 May ... ... ... ... | 1,221,000 | 1,500,500 |
| 1921 June ... ... ... ... | 1,065,000 | 1,192,000 |

Both countries were feeling the effects of general world depression and of price-cutting by Belgian and German competitors. Under these influences makers of pig-iron in this country are at present quoting prices as low as £8 10s. per ton. After the first few weeks of the coal dispute, practically every blast furnace in the country was closed down, but with the close of the coal dispute, a slow recovery is now expected, although its course is dependent on a moderate price of coal.—*Board of Trade Journal.*

TELLURIUM TETRAIODIDE.—Its existence, long doubted, has been demonstrated by M. Damiens. It is in form of small black brilliant crystals, 4 to 5 mm. long. Density at +15° is 5·05. Little soluble in alcohol and acetone, it is insoluble in ether, chloroform, and carbon sulphide. Though proof against humid air, it is slowly attacked by cold water, and decomposition in hot water liberates hydroiodic acid almost immediately decomposed. It is suitable for preparation of numerous derivatives of tellurium, but its speedy decomposition restricts the chemical actions in view to low temperatures.—*Comptes Rendus*, May, 1921.

AMERICAN CHEMICAL SOCIETY.—The Fall Meeting of the American Chemical Society will be held with the New York Section, Tuesday, September 6 to Saturday, September 10. This will probably be the largest Meeting of the American Chemical Society that has ever been held. Aside from the 2500 members of the New York Section itself, many thousands are within a four or five hours' ride of New York. In addition to the usual features, we shall have as guests at this time a considerable number of British and Canadian members of the Society of Chemical Industry, who will have held their Annual Meeting in Canada, will be greeted at the border by the Governor of the State, and will arrive in New York on Wednesday morning, September 7. After being the guests of the American Section of the Society of Chemical Industry at a luncheon on September 7, they then become the guests of the American Chemical Society for the remainder of the week. We expect three or four hundred of these British and Canadian friends, besides three or four thousand from the American Chemical Society. All members of the American Chemical Society are invited to the meeting in Montreal, beginning August 29. A further reason for this being a large and successful meeting is the opening of the National Exposition of Chemical Industries on September 12, immediately after the close of our meeting. A great many guests from all over the United States who visit this Exposition each year, will come a few days earlier to attend the Meeting of the American Chemical Society.

MR. DOUGLAS H. INGALL, M.Sc., chief assistant to Prof. Turner, Birmingham University, has been appointed Principal of the County Technical College, Wednesbury, in succession to Mr. Walter Macfarlane, F I.C., who now retires as Emiritus Principal after 25 years service with the Staffordshire Education Committee.

DISTILLATION OF THE LEAVES OF GREEN PLANTS. —The distillation of the leaves, immediately after gathering without addition of water, under reduced pressure at 60° C., gives ethyl alcohol, acetic aldehyde, nitrous acid. The experimenter, M. Mazé, did not find formic aldehyde. The leaves of the haricot and maize contain, in very fine weather, acetylmethylcarbinol, those of the elder free hydrocyanic acid and glycolic aldehyde, those of the poplar lactic aldehyde. Formation of acetylmethylcarbinol, glycolic and lactic aldehydes is closely allied with assimilation of carbonic acid Maize and haricot leaves are destitute of acetylmethylcarbinol in the morning, but contain it in increasing quantities during days of sunshine; on rainy and cold days they are completely destitute. Haricot leaves contain coumarine in the evening and not in the morning. —*Comptes Rendus*, clxxi., No. 26.

CALCIC CYANAMIDE.—The first idea of manufacture of calcic cyanamide is due to Berthelot, then Franck and Caro. It was produced on an industrial scale in Italy subsequently, the carbide being treated in retorts superheated on the exterior with nitrogen. The yield was bad, owing to superheating against the sides. It was then noted that the reaction being exothermic, it sufficed to heat the mass at one point to 800° to 1000° C. to start the reaction. This heating was first obtained with a carbon heated by electricity. In the more recently constructed plant, electricity is yet utilised, but for heating on the circumference, which gives a better start to the reaction. Trials have also been made with tunnel kilns, but in spite of great improvements, nothing very satisfactory has been obtained. Thus a product with 19 to 22 per cent nitrogen is produced, whereas theory gives 30 per cent; the impurities are mainly lime, carbon, and unattacked carbide. It is estimated that 1700 kilogrms. of cyanamide with 20 per cent nitrogen can be manufactured with

1 H.P. Cyanamide, with the water of the soil, gives urea, and then carbonate of ammonia, which are oxidised by nitrifying bacteria into directly assimilable nitrates. For employment in agriculture it is hydrated to destroy quick-lime and carbide, then granulated as far as possible to prevent formation of dangerous dust. Unfortunately, a really practical method of granulation has not yet been found. Cyanamide can also be mixed with other fertilisers like superphosphates taking certain precautions to prevent retrogradation.—*L'Engrais*, June 3, 1921.

## New Patents.

THIS List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

19376—Badische Anilin & Soda Fabrik.—Production of thymol. July 18.

19531—Dreyfus, H.—Manufacture of solutions, compositions, preparations, of articles of cellulose derivatives. July 20.

19669—Gluud, W. W.—Method of extracting sulphuretted hydrogen from gases. July 21.

19848—Scottish Dyes, Ltd.—Colouring matters of the napththalene series. July 23.

*Specifications published this Week.*

166228—Marks, E. C. R.—Recovery of fluorine as hydrofluoric acid.

166289—Head, C. J.—Process for the manufacture of chromic oxide and sodium sulphide from sodium chromate.

166425—Renck, ..—Production of casts from ferrous sulphide.

145053—Akt Ges. für Anilin-Fabrikation.—Manufacture of ortho-oxy-ayo-disayo-dye-stuffs.

*Abstract Published this Week.*

*Purifying Fats, Etc.*—Patent No. 164115.—Mr. H. Bolman of 1, Alsterdamm, Hamburg, Germany, has obtained a Patent for an improved process of purifying fats and fatty oils from fatty acids, resins, mucilaginous and bitter substances, etc., by treatment in counter current with a solvent for fatty acids, etc., but not for glycerides. A series of extraction vessels is used, and the solvent and fatty oil are separated from each other before passing to the next vessels. Solvents specified are methyl alcohol, ethyl alcohol, amyl alcohol, acetone, acetic ester, diluted or not with water to ensure a sufficient difference in the specific gravity of the solvent and of the oil. When fats are treated, the temperature is maintained sufficiently high to ensure liquefaction. In the apparatus, rape or other oil from a reservoir, is passed continuously into the highest vessel of a series of washing vessels, and three times the volume of 96 per cent alcohol from a reservoir into the lowest vessel, while the agitator works continuously. The mixture in each vessel passes continuously to a separator opposite by pipes, and separates into two layers, the alcoholic solution from other separators passing respectively to washing vessels, and that from another separator through a pipe to a still, while the oily lower layer passes from separators to washing vessels and that from another separator to a still for the removal of residual alcohol. A temperature of 20-30° C. is maintained throughout. In a modified apparatus, treatment and separation take place in the one series of vessels, no agitators being employed, but retarding means such as Raschig rings, are used to ensure mixing and separation, and the separated oil and solvent flow to the next vessels through siphons.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.



## NOTICES.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THE CHEMICAL NEWS.
VOL. CXXIII., No. 3201.

## COAL WASTAGE IN TANK BOILERS.
### Its Causes and Prevention.

By W. H. CASMEY, of Holdsworth & Sons, Ltd., Bradford.

The wastage of human life and coal are caused by neglecting the laws of combustion, and consequently such losses are preventable, the loss of life being due to lack of air, and that of coal wastage for the very opposite reason—too much air.

Whatever types of tank boilers are used, Cornish, Lancashire, or Yorkshire, the factors governing their duty and efficiency are:—

(*a*) The correct proportion of air and coal to give the highest workable furnace temperature, approximately 2750° F.

(*b*) A standard ratio of 2 to 1 between the size of grates and smallest section area through which the products of combustion are to pass, between the ends of the furnaces and chimney bottom; depth of bottom flue half diameter of boiler; width of side flues one-seventh diameter of boiler.

With the above conditions and a minimum of brains between the coal heap and boiler furnaces, there will be no difficulty in securing an overall efficiency of 80 per cent or even more; there are of course, many minor details to consider, but every works engineer knows his own plant, and should be fully capable of dealing with it successfully, and the purport of this article is to show in a simple practical way, how, if we but get hold of the governing principle of economical steam production, we can not only save coal, but produce healthier surroundings for all.

The Law of Mathematics shows that twice 2 equals 4, and that 4 times 9 equals 36, and no argument can change the results; if, however, we make an error in our calculations, giving the answer as 35 instead of 36, we at once blame ourselves for the mistake, and not the mathematical rule, and this is the method to adopt in the boiler house, which is self-evident from the following illustrations.

To burn 1lb. of ordinary steam coal so that no waste shall take place requires 12lb. of air, and these elements combined give a $CO_2$ reading of 19·2 per cent, the furnace temperature being 4000°; and it is well to remember that the temperature of combustion is a constant, but much too high for steam raising purposes.

For good steam practice, the theoretical weight of air should be increased 50 per cent, thus making the proportions of 18lb. of air to 1lb. of coal; but this additional 6lb. of air, as already inferred, does not affect the temperature of combustion, but at once reduces the temperature of the furnaces from 4000° to a workable and useful temperature of, say, 2750°, and in this case the products of combustion contain 13 per cent $CO_2$; therefore, by increasing the air supply 6lb., the $CO_2$ is reduced 6·2 per cent, and that of the temperature 1300°.

Experience indicates, however, that in general practice we allow about 30lb. of air per lb. of coal, and with this 12lb. additional air supply, the $CO_2$ is only 7 per cent, and the furnace temperature 1750°, showing in this case the additional 12lb. of air reduces the $CO_2$ a further 6 per cent, and the furnace temperature an additional 1000°; it is therefore nothing besides pure neglect in not attending to the supplies of air and coal delivered to the furnaces being proportional for practical combustion, which causes fuel wastage.

Assuming we are working a boiler at 120lb. working pressure, the temperature of the steam will be 350°, and with 18lb. of air per lb of coal the difference in temperature between the water side and fire side of the boiler plates will be 2350°; but with air and coal in the proportion of 30 to 1 the difference will be only 1400°, which in practice means that one square foot of grate in the first case radiates as much heat per unit of time as 2¼ square feet will radiate in the second case, and which can be further illustrated by saying, with the 18 to 1 proportions of air and coal, 15cwt. of coal will evaporate as much water as 20cwt. will do when the air and coal are in proportion of 30 to 1.

Briefly, the furnace temperature is always proportionate to the ratio between the air and coal supplied, and the heat transmitted to the water governed by such temperature; we therefore have practical demonstration that the chief factor contributing to coal wastage is excess air over that required for practical combustion, and economy will be secured when the same care is taken in producing heat as in producing every article we manufacture, *i.e.*, correct proportions and the results will then be right every time.

In working any steam plant, or even when attending to the domestic fires, this broad fact should be recognised, that the first gases liberated from a new charge of coal will not ignite at a lower temperature than 900°; therefore stoking should be done when the fires are clear and bright, and it will be found impossible to then produce black smoke; in fact, the emission of smoke from a chimney top spells inefficiency at the chimney bottom. Black smoke, it may also be useful to remember, contains two grains of carbon per cubic foot of gases, and as generally 400 cubic feet of air is supplied per lb. of coal, black smoke takes away about 11 per cent of the coal used, *i.e.*, during a black smoke period.

Instead of the conditions briefly indicated as necessary for giving an overall efficiency of 80 per cent, it is generally found that the boiler house is the one place where chaos reigns supreme, as boiler efficiencies range from less than 50 per cent to over 80 per cent; the latter figure will be attained by probably not more than 3 per cent of our steam plants, throughout the country the average of which probably does not exceed 60 per cent, indicating an annual loss of nearly 50 million tons of coal, and the cause of this huge wastage, as before stated, is due to more excess air than to careless stoking, such excess being caused by conditions over which the boiler attendant has no control.

It will be quite clear, even to the lay mind, that the weight of coal burned in a given time is governed by the weight of air passing through the furnaces in that time, and yet we find that a Lancashire boiler 7ft. diameter has 4 sq. feet of grate area to each square foot of outlet for the products of combustion to pass through; that a similar type of boiler 8ft. diameter has a ratio

of 3·5 to 1, and in a boiler 9ft. diameter, the ratio is 2·7 to 1, and if the 4 to 1 ratio is correct, the other two must be wrong.

The reason for these variable proportions between areas of furnaces and outlets for the gases was brought about by the introduction of tapering the back ends of the furnace flues 50 years ago, and which has had the effect of not only reducing the duty of the boiler, but also its efficiency by making it possible for 2·7 square feet of grate in one boiler to burn as much coal as 4 square feet in another of the same type, though the chimney draught is the same.

Years of experience have proved that the correct ratio between grate areas and outlets from the furnace flues for the products of combustion should not exceed 2 to 1, and under such conditions each square foot of grate in a 7ft. diameter Lancashire boiler would give the same evaporation as 1 square foot of grate in a boiler 9ft. in diameter, and the same applies to Lancashire boilers of all sizes, hence the need for establishing a fixed standard of grate suitable for boilers of all diameters, as is done in the Yorkshire boiler with most satisfactory results, both in duties and efficiencies each square foot of grate in any sized boiler giving equal evaporation.

We know the proportions of air and coal for producing a given temperature; we know the ratio between grate and outlet from the boiler for the products of combustion to pass through for securing this temperature, and that heat transmission is proportional to the difference in temperature between the furnace and fire sides of the boiler plates; also that a square foot of plate transmits double the number of heat units in a unit of time when the water above it is actively boiling, than when stagnant. Knowing these facts and others, such as radiation, &c., there is no excuse for wasted coal, and if the recent stoppage of the coal mines has taught us the value of burning coal correctly, the country will eventually benefit, though the lesson has been a most expensive one.

## A NEW PHOTOGRAPHIC METHOD OF RENDERING THE SOLIDITY OF OBJECTS IN SPACE.

### (PHOTO-STEREO-SYNTHESIS).

By F. F. RENWICK, A.C.G.I., F.I.C., F.R.P.S.

Monsieur Louis Lumiere, to whom photographic science and practice are already deeply indebted for several epoch-making inventions, chief among which may be mentioned the practical realisation of kinematography and the invention of the famous Autochrome colour plate, has recently worked out an entirely novel method of obtaining photographic reproductions of solid objects which give remarkably lifelike impressions of relief. Hitherto the only satisfactory method of doing this was by the aid of the stereoscopic camera and stereoscope. Monsieur Lumière's new method is unlikely to become popular, but is undoubtedly very ingenious, and possesses great scientific interest, so that the striking example of his work which the Scientific and Technical Group Committee has been able to obtain from Monsieur Lumière for display at the Society's forthcoming Exhibition will be sure to excite attention both of members and of the general public. The fact that the specimen so kindly lent us is a portrait of the Postmaster-General, Mr Kellaway, taken on the occasion of his visit to the Lyons Fair, will also doubtless add to the interest of the exhibit.

The means by which these pictures are made was described in a communication to the French Academy of Sciences in November last, and published in the *Comptes Rendus* (clxxi., 891), and a translation of this paper appeared in the *British Journal of Photography* for February 25 last (lviii., 110), so that it is unnecessary to describe the method in detail. The principle of the method, however, consists in the taking of a succession of photographs with a special camera, whose lens and plate-holder are both kept moving during each exposure. The motion of the sensitive plate is so adjusted to that of the lens that the images of all objects in one particular plane remain stationary on the sensitive plate, while the unsharp images of objects in other planes, before or behind this, move to a greater or less extent, and so fail to produce a recognisable image on the plate. The lens is first sharply focussed and exposure made on the part of the object nearest the camera, and then, before each succeeding exposure, the camera is moved bodily forward on rails so as to bring into sharp focus a somewhat deeper plane of the object, till the whole thickness of it has been dealt with.

In practice, Monsieur Lumière has used 18×24 cm. plates, and produces bust portraits half life-size. The lens is carried by a star-shaped panel, and is given a circular motion of 8 cm. diameter by the revolution of four cranks and spindles when driven by the simple belt and pulley arrangement. Somewhat longer cranks at the back of the camera carry the plate-holder, which is revolved in a circle of 12 cm. diameter by the same means.

In the case of a half-size portrait like that of Mr. Kellaway, Monsieur Lumière finds that six successive exposures suffice to give a satisfactory rendering of solidity.

From these negatives six very thin positives are made and arranged one behind another in a grooved frame in proper order and correctly spaced in accordance with the advances made by the camera between the successive exposures. A diffusing glass behind the asemblage of positives serves to produce even illumination from a lamp at the back of the whole.

To view the picture properly, it is necessary to stand straight in front of it and to direct the gaze normally to the surface from a distance of several feet. In addition to the method by which this and other similar portraits have been produced, Monsieur Lumière has also described another most interesting means by which these striking effects of solid relief could be produced. This second method, which is also described in the original paper referred to, is remarkably interesting for the reason that it foreshadows the possibility of producing full scale copies of maps, drawings, or other plane surfaces of any size with a small lens. Owing to the fact that sufficiently accurately made Porro prisms were not available, Monsieur Lumière failed to get satisfactory results by this method, but it is to be hoped that one or other of our skilled optical instrument makers will undertake their production and open up the new possibilities which the idea appears to offer.—*Photographic Journal*, August, 1921.

# THE RELATIVE VOLUMES OF THE CHEMICAL ELEMENTS.

By HAWKSWORTH COLLINS. Continued from Vol. cxxii., p 77.

THIRD deduction.—The experimental facts concerning the following 76 molecules demonstrate that one relative volume of H is 15·25 at 15° C., for, whether Cl, Br, I, $NH_2$, $NO_3$, SH, $C_2H_3$, $C_2H$, $CO_2CH_3$, $CO_2C_2H_5$, $CO_2C_3H_7$, $CO_2H$ or OH (13·29) in such molecules as those numbered 1—115 be displaced by H, the volume of this H-atom is always the same.

| | Name | Chem. formula | Vols. of parts | Theor. S.G. | Observed S G | |
|---|---|---|---|---|---|---|
| 50 | Me Cl | $H—CH_2—Cl$ | 15·25—(16·42)—23·01 | 0·924 | 0·920 18° Vi. | 0·929 13° Vi |
| | Et Cl | $H—(CH_2)_2—Cl$ | 15·25—$(16·42)_2$—23·01 | 0·907 | 0·851 12° Rm. | 0·923 15° P |
| | Pr Cl | $H—(CH_2)_3—Cl$ | 15·25—$(16·42)_3$—23·01 | 0·897 | 0·896 19° L. | 0·893 15° P |
| | But Cl | $H—(CH_2)_4—Cl$ | 15·25—$(16·42)_4$—23·01 | 0·890 | 0·887 20° Lb. | 0·897 14° L |
| | n-Pent Cl | $H—(CH_2)_5—Cl$ | 15·25—$(16·42)_5$—23·01 | 0·885 | 0·883 20° Lb. | 0·896 0° Pr |
| | Hep Cl | $H—(CH_2)_7—Cl$ | 15·25—$(16·42)_7$—23·01 | 0·878 | 0·874 18° Sc. | ∴ 0·877 15° |
| 55 | Oc Cl | $H—(CH_2)_8—Cl$ | 15·25—$(16·42)_8$—23·01 | 0·876 | 0·878 15° P. | 0·850 C. |

In the following M stands for methylene ($CH_2$) both in the formula and in the relative volume. Its volume is always 16·42.

| | Name | Chem. formula | Vols. of parts | Theor. S.G. | Observed S G | |
|---|---|---|---|---|---|---|
| | Et Br | $H—M_2—Br$ | $15·25—M_2—27·00$ | 1·438 | 1·450 15° P. | 1·419 15° M |
| | Pr Br | $H—M_3—Br$ | $15·25—M_3—27·00$ | 1·333 | 1·350 0° Pr | ∴ 1·333 15° |
| | But Br | $H—M_4—Br$ | $15·25—M_4—27·00$ | 1·260 | 1·260 14° Dh. | |
| 160 | Am Br | $H—M_5—Br$ | $15·25—M_5—27·00$ | 1·206 | 1·206 15·7° M | |
| | Hep Br | $H—M_7—Br$ | $15·25—M_7—27·00$ | 1·132 | 1·133 16° Cs. | |
| | Ethyl I | $H—M_2—I$ | $15·25—M_2—32·75$ | 1·930 | 1·931 15° M. | 1·931 14° G. |
| | Prop I | $H—M_3—I$ | $15·25—M_3—32·75$ | 1·748 | 1·748 14° Dh. | 1·747 16° L |
| | Butyl I | $H—M_4—I$ | $15·25—M_4—32·75$ | 1·619 | 1·617 20° B. | |
| | n-Pent I | $H—M_5—I$ | $15·25—M_5—32·75$ | 1·522 | 1·517 20° Lb. | ∴ 1·522 15° |
| 165 | Hexyl I | $H—M_6—I$ | $15·25—M_6—32·75$ | 1·447 | 1·466 0° Db. | ∴ 1·448 15° |
| | Hept I | $H—M_7—I$ | $15·25—M_7—32·75$ | 1·387 | 1·401 0° Db. | ∴ 1·383 15° |
| | Octyl I | $H—M_8—I$ | $15·25—M_8—32·75$ | 1·338 | 1·338 16° Zi. | |
| | Nonyl I | $H—M_9—I$ | $15·25—M_9—32·75$ | 1·297 | 1·287 16° Kr. | |
| | Decyl I | $H—M_{10}—I$ | $15·25—M_{10}—32·75$ | 1·263 | 1·287 0° Kr | 1·260 16° Kr. |
| 170 | Et Amine | $H—M_2—NH_2$ | $15·25—M_2—16·42$ | 0·698 | 0·696 8° W. | 0·699 8° Va |
| | But amine | $H—M_4—NH_2$ | $15·25—M_4—16·42$ | 0·75 | 0·7553 0° Lb. | |
| | Amyl amine | $H—M_5—NH_2$ | $15·25—M_5—16·42$ | 0·765 | 0·772 0° Pl. | ∴ 0·762 15° |
| | Hex amine | $H—M_6—NH_2$ | $15·25—M_6—16·42$ | 0·776 | 0·768 17° Pe | ∴ 0·77 15° |
| 175 | Oct amine | $H—M_8—NH_2$ | $15·25—M_8—16·42$ | 0·79 | 0·786 Sq | |
| | M-nitril | $H—M_{13}—CN$ | $15·25—M_{13}—23·96$ | 0·827 | 0·828 19° Kr. | 0·824 25° Kr. |
| | Pl-nitril | $H—M_{15}—CN$ | $15·25—M_{15}—23·96$ | 0·830 | 0·822 31° Kr. | 0·776 99° Kr<br>∴ 0·830 15° |
| | Ste-nitril | $H—M_{17}—CN$ | $15·25—M_{17}—23·96$ | 0·833 | 0·818 41° Kr | 0·779 99° Kr<br>∴ 0·835 15° |
| | Me triaz | $H—M—N_3$ | $15·25—M—32·63$ | 0·89 | 0 896 8° Va. | ∴ 0·891 15° |
| 180 | Et nitrate | $H—M_2—NO_3$ | $15·25—M_2—34·27$ | 1·105 | 1·104 25° K. | 1·113 15° Ko |
| | Pr nitrate | $H—M_3—NO_3$ | $15·25—M_3—34·27$ | 1·063 | 1·063 15° Va. | |
| | Et mercap | $H—M_2—SH$ | $15·25—M_2—25·48$ | 0·843 | 0·842 15° Ze. | 0·839 20° N |
| | But mercap | $H—M_4—SH$ | $15·25—M_4—25·48$ | 0·846 | 0·843 16° Gr. | 0·858 0° Gr |
| | Am mercap | $H—M_5—SH$ | $15·25—M_5—25·48$ | 0·847 | 0·840 17° Ko. | 0·848 13° BH |
| 185 | Et acetate | $H—M_2—CO_2CH_3$ | $15·25—M_2—49·71$ | 0·900 | 0·901 20° B. | 0·898 15° M |
| | Pr acetate | $H—M_3—CO_2CH_3$ | $15·25—M_3—49·71$ | 0·893 | 0·899 15° L. | 0·885 20° B |
| | Bu acetate | $H—M_4—CO_2CH_3$ | $15·25—M_4—49·71$ | 0·888 | 0·882 20° Lb. | 0·900 0° Lb |
| | n-Am acet | $H—M_5—CO_2CH_3$ | $15·25—M_5—49·71$ | 0·884 | 0·896 0° Lb. | ∴ 0·884 15° |
| | n-Hex acet | $H—M_6—CO_2CH_3$ | $15·25—M_6—49·71$ | 0·881 | 0·890 0° Ga. | ∴ 0·88 15° |
| 190 | n-Hep acet | $H—M_7—CO_2CH_3$ | $15·25—M_7—49·71$ | 0·878 | 0·874 16° Cs. | 0·889 0° Ga |
| | n-Oct acet | $H—M_8—CO_2CH_3$ | $15·25—M_8—49·71$ | 0·876 | 0·885 0° Ga. | ∴ 0·875 15° |
| | Me pelarg | $H—M_8—CO_2CH_3$ | $15·25—M_8—49·71$ | 0·876 | 0·876 17° Zi. | |
| | Et propion | $H—M_2—CO_2C_2H_5$ | $15·25—M_2—66·13$ | 0·893 | 0·894 17° L. | 0·891 15° Ir |
| | Et butyr | $H—M_3—CO_2C_2H_5$ | $15·25—M_3—66·13$ | 0·888 | 0·899 0° El. | ∴ 0·888 15° |
| 195 | Pr propion | $H—M_3—CO_2C_2H_5$ | $15·25—M_3—66·13$ | 0·888 | 0·888 13° L. | |
| | Et valerate | $H—M_4—CO_2C_2H_5$ | $15·25—M_4—66·13$ | 0·884 | 0·894 0° Lb | 0·878 18° C |
| | Bu propion | $H—M_4—CO_2C_2H_5$ | $15·25—M_4—66·13$ | 0·884 | 0·883 15° L. | |
| | Am propion | $H—M_5—CO_2C_2H_5$ | $15·25—M_5—66·13$ | 0·881 | 0·888 0° El. | |
| | Et capro | $H—M_5—CO_2C_2H_5$ | $15·25—M_5—66·13$ | 0·881 | 0·878 19° C. | ∴ 0·881 15° |
| 200 | Et oenanth | $H—M_6—CO_2C_2H_5$ | $15·25—M_6—66·13$ | 0·878 | 0·877 16·5° C. | ∴ 878 15° |
| | Et capryl | $H—M_7—CO_2C_2H_5$ | $15·25—M_7—66·13$ | 0·876 | 0·874 15° Fe. | 0·878 17° C |
| | n-Hep prop | $H—M_7—CO_2C_2H_5$ | $15·25—M_7—66·13$ | 0·876 | 0·885 0° Ga. | ∴ 0·874 15° |

ABBREVIATIONS.—Ah, Ahrers; Ar, Arnheim; Bb, Barbier; BH, Biochem Handlexicon, Bl, Beilstein, Cs, Cross, Cu, Claus; Db, Dobriner, El, Elsasser; Fe, Fehling; Fi, Fischer, Gr, Grabowski; Ht, Holtmeyer; Ir, Israel, Ja, Jacobsen; Kg, Kruger, Kn, Korner, Kr, Kraut, Lf, Lefebvre, Lc, Lachowicz, Lm, Lemoine; LB, Le Bas; N, Nasini; Na, Naquet; No, Nolting, Pe, Pelouze; Pp, Philip; Pr, Pierre, Ps, Petersen; Py, Parry; Rd, Rudorff, Rm, Ramsay; Rn, Renard; Scm, Schramm, Sd, Stadeler, Se, Schwanert; Sf, Senff; Sp, Schepper; Sq, Squire, Sz, Schweinitz; Ta, Tawildarow; Vi, Vincent; Wa, Warren; Wk, Walker; Ze, Zeise, Zi, Zincke.

| | Name | Chem. formula | Vols. of parts | Theor. S.G. | Observed S.G. | |
|---|---|---|---|---|---|---|
| | Et pelarg | $H—M_8—CO_2C_2H_5$ | 15·25—$M_8$—66·13 | 0·874 | 0·873 15° De. | |
| | n-Oc prop | $H—M_8—CO_2C_2H_5$ | 15·25—$M_8$—66·13 | 0·874 | 0·883 0° Ga. | ∴ 0·873 15° |
| 205 | Et laurate | $H—M_{11}—CO_2C_2H_5$ | 15·25—$M_{11}$—66·13 | 0·870 | 0·867 19° De. | ∴ 0·870 15° |
| | n-Hep butyr | $H—M_7—CO_2C_3H_7$ | 15·25—$M_7$—82·55 | 0·874 | 0·883 0° Ga. | .. 0·872 15° |
| | Pr butyr | $H—M_3—CO_2C_3H_7$ | 15·25—$M_3$—82·55 | 0·884 | 0·893 0° El. | 0·879 15° L. |
| | Pr capro | $H—M_3—CO_2C_5H_{11}$ | 15·25—$M_{11}$—115·39 | 0·878 | 0·884 0° Ga. | ∴ 0·873 15° |
| | Butyl alc | $H—M_4—OH$ | 15·25—$M_4$—10·21 | 0·812 | 0·811 15° L. | 0·810 20° B |
| 210 | Amyl alc | $H—M_5—HO$ | 15·25—$M_5$—10·21 | 0·818 | 0·818 15° C. | 0·818 14° De |
| | Hexyl alc | $H—M_6—HO$ | 15·25—$M_6$—10·21 | 0·823 | 0·820 20° Lb. | ∴ 0·823 15° |
| | Heptyl alc | $H—M_7—HO$ | 15·25—$M_7$—10·21 | 0·826 | 0·819 23° Sd. | 0·830 16° Cs |
| | Octyl alc | $H—M_8—HO$ | 15·25—$M_8$—10·21 | 0·829 | 0·830 16° Zi. | 0·837 0° Z |
| | Nonyl alc | $H—M_9—HO$ | 15·25—$M_9$—10·21 | 0·831 | 0·835 10° Kr. | 0·828 20° Kr |
| 215 | Decyl alc | $H—M_{10}—HO$ | 15·25—$M_{10}$—10·21 | 0·833 | 0·830 20° Kr. | ∴ 0·833 15° |
| | Dod ec alc | $H—M_{12}—HO$ | 15·25—$M_{12}$—10·21 | 0·836 | 0·831 24° Kr. | ∴ 0·836 15° |
| | n-Alcohol | $H—M_{14}—HO$ | 15·25—$M_{14}$—10·21 | 0·838 | 0·824 38° Kr. | 0·815 50° Kr<br>∴ 0·838 15° |
| | n-Alcohol | $H—M_{16}—HO$ | 15·25—$M_{16}$—10·21 | 0·840 | 0·810 60° Kr. | 0·784 99° Kr<br>∴ 0·840 15° |
| | n-Alcohol | $H—M_{18}—HO$ | 15·25—$M_{18}$—10·21 | 0·841 | 0·812 59° Kr. | 0·785 99° Kr<br>∴ 0·841 15° |
| 220 | Myris acid | $H—M_{13}—CO_2H$ | 15·25—$M_{13}$—23·80 | 0·903 | 0·862 54° Va. | ∴ 0·90 15° |
| | Palm acid | $H—M_{15}—CO_2H$ | 15·25—$M_{15}$—23·80 | 0·897 | 0·846 76° Va. | ∴ 0·89 15° |
| | Stear acid | $H—M_{17}—CO_2H$ | 15·25—$M_{17}$—23·80 | 0·893 | 0·852 69° Sh. | 0·843 80° Va<br>∴ 0·899 15° |
| | Cerot acid | $H—M_{25}—CO_2H$ | 15·25—$M_{25}$—23·80 | 0·881 | 0·836 70° Va. | ∴ 0·88 15° |
| | Heptidene | $H—M_5—C_2H$ | 15·25—$M_5$—31·25 | 0·746 | 0·746 20° B. | |
| 225 | Conylene | $H—M_6—C_2H$ | 15·25—$M_6$—31·25 | 0·76 | 0·76 CK. | 0·770 0° Va |

Fourth Deduction.—The experimental facts concerning the following 24 molecules demonstrate that another relative volume of H is 12·22 at 15° C., for, whether Cl, Br, I, $NH_2$, CN, $N_3$, $NO_3$, SH, $CO_2CH_3$, $CO_2C_2H_5$, $CO_2C_3H_7$, OH(10·21), $C_2H$ or $CO_2H$ be displaced by H in such molecules as those numbered 150—225, the relative volume of the H-atom is always the same.

*The Paraffins.* M stands for methylene (16·42).

| | Formula | Vols. of parts | Theor S.G. | Observed S.G. | | |
|---|---|---|---|---|---|---|
| | $H—M_3—H$ | 15·25—$M_3$—12·22 | 0·573 | 0·613 −25° Lf. | | ∴ 0·58 15° |
| | $H—M_4—H$ | 15·25—$M_4$—12·22 | 0·623 | 0·624 −1° Lf. | | |
| | $H—M_6—H$ | 15·25—$M_6$—12·22 | 0·683 | 0·678 15° Sc. | 0·698 14° Lc. | |
| | $H—M_7—H$ | 15·25—$M_7$—12·22 | 0·702 | 0·702 14° Lc. | | |
| 230 | $H—M_8—H$ | 15·25—$M_8$—12·22 | 0·718 | 0·719 17° Sc. | 0·716 15° T. | |
| | $H—M_9—H$ | 15·25—$M_9$—12·22 | 0·730 | 0·731 16° Lm. | 0·733 0° LB. | |
| | $H—M_{10}—H$ | 15·25—$M_{10}$—12·22 | 0·741 | 0·732 20° Lc. | 0·753 16° Lm. | |
| | $H—M_{11}—H$ | 15·25—$M_{11}$—12·22 | 0·750 | 0·745 15° Kr. | 0·758 20° Va. | |
| | $H—M_{12}—H$ | 15·25—$M_{12}$—12·22 | 0·757 | 0·755 15° Kr. | 0·768 20° Va. | |
| 235 | $H—M_{13}—H$ | 15·25—$M_{13}$—12·22 | 0·764 | 0·761 15° Kr. | | |
| | $H—M_{14}—H$ | 15·25—$M_{14}$—12·22 | 0·769 | 0·768 15° Kr. | 0·775 5° Kr. | |
| | $H—M_{15}—H$ | 15·25—$M_{15}$—12·22 | 0·774 | 0·772 15° Kr. | | |
| | $H—M_{16}—H$ | 15·25—$M_{16}$—12·22 | 0·779 | 0·775 18° Kr. | | |
| | $H—M_{17}—H$ | 15·25—$M_{17}$—12·22 | 0·783 | 0·776 22° Kr. | 0·771 30° Kr. | ∴ 0·782 15° |
| 240 | $H—M_{18}—H$ | 15·25—$M_{18}$—12·22 | 0·786 | 0·777 28° Kr. | | ∴ 0·786 15° |
| | $H—M_{19}—H$ | 15·25—$M_{19}$—12·22 | 0·789 | 0·777 32° Kr. | 0·772 40° Kr. | ∴ 0·789 15° |
| | $H—M_{20}—H$ | 15·25—$M_{20}$—12·22 | 0·792 | 0·778 37° Kr. | 0·749 80° Kr. | ∴ 0·792 15° |
| | $H—M_{21}—H$ | 15·25—$M_{21}$—12·22 | 0·795 | 0·778 40° Kr. | 0·740 99° Kr. | ∴ 0·795 15° |
| | $H—M_{22}—H$ | 15·25—$M_{22}$—12·22 | 0·798 | 0·778 44° Kr. | 0·742 99° Kr. | ∴ 0·799 15° |
| 245 | $H—M_{23}—H$ | 15·25—$M_{23}$—12·22 | 0·800 | 0·778 47° Kr. | 0·746 99° Kr. | ∴ 0·800 15° |
| | $H—M_{24}—H$ | 15·25—$M_{24}$—12·22 | 0·802 | 0·779 51° Kr. | 0·748 99° Kr. | ∴ 0·802 15° |
| | $H—M_{27}—H$ | 15·25—$M_{27}$—12·22 | 0·807 | 0·780 59° Kr. | 0·754 99° Kr. | ∴ 0·809 15° |
| | $H—M_{31}—H$ | 15·25—$M_{31}$—12·22 | 0·813 | 0·781 68° Kr. | 0·762 99° Kr. | ∴ 0·817 15° |
| | $H—M_{32}—H$ | 15·25—$M_{32}$—12·22 | 0·814 | 0·781 70° Kr. | | ∴ 0·817 15° |

Fifth Deduction.—Methyl has the volume 31·67 (=16·42+15·25) at one end of a carbon chain, and the volume 28·64 (=16·42+12·22) at the other end.

Sixth Deduction.—When an atom of hydrogen, whose volume is 15·25, is displaced by $CH_3$, the volume of the latter is 16·42+15·25; and when an atom of H, whose volume is 12·22, is displaced by $CH_3$, the volume of the latter is 16·42+12·22.

Seventh Deduction.—The two valencies of carbon so far concerned are distinguished from one another by the fact that H has the volume 15·25 in one position, and 12·22 in the other. (The former will be called the "first position," and the latter the "second position.").

As said before, it is evident that perfect regularity in the relative volumes of molecules exists at the temperature of 15° C.; so that it is quite plain that Kopp's very inaccurate conclusions with regard to the relative volumes of molecules at their various boiling points have misled scientists for more than half-a-century.

It is necessary to remember that it is impossible to find exact regularity in 250 molecules, if it is not really there to be discovered.

There is, no other explanation possible of the above results than that an atom of hydrogen occupies a volume of 15·25 in the first position of the carbon atom, and of 12·22 in the second position.

If chemists like to consider that these two volumes include co-volumes, they must then admit that these atoms are differentiated by their co-volumes.

The exact volumes of the two H-atoms in methylene ($CH_2$) will be shown later, and it will then be seen that the four valencies of carbon can easily be differentiated. They will also be differentiated in other ways.

The doctrine that the four valencies of carbon are indistinguishable from one another is the greatest stumbling-block that has ever been placed in the way of scientists, and accounts for the apparently inextricable confusion in the higher regions of chemistry.

This matter will be kept absolutely free from conjecture, and every deduction which is demonstrated will be supported by overwhelming evidence obtained from the experimental numerical data of other men.

When the same individual both performs the experiments and also reasons upon the results, there is a danger that his experimental figures may be unconsciously influenced by his preconceived ideas.

(To be continued).

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IN a paper in the *Philosophical Magazine* for May last, Mr. A. H. Compton describes a new method for the calculation of short wave-lengths by which he has been able to measure the wave-length of Hard Gamma Rays, the value determined for rays that have passed through 8 mm. of lead is from 0·025 to 0·030 Angström units.

## THE BEHAVIOUR OF SUBSTANCES NEAR THE ABSOLUTE ZERO.

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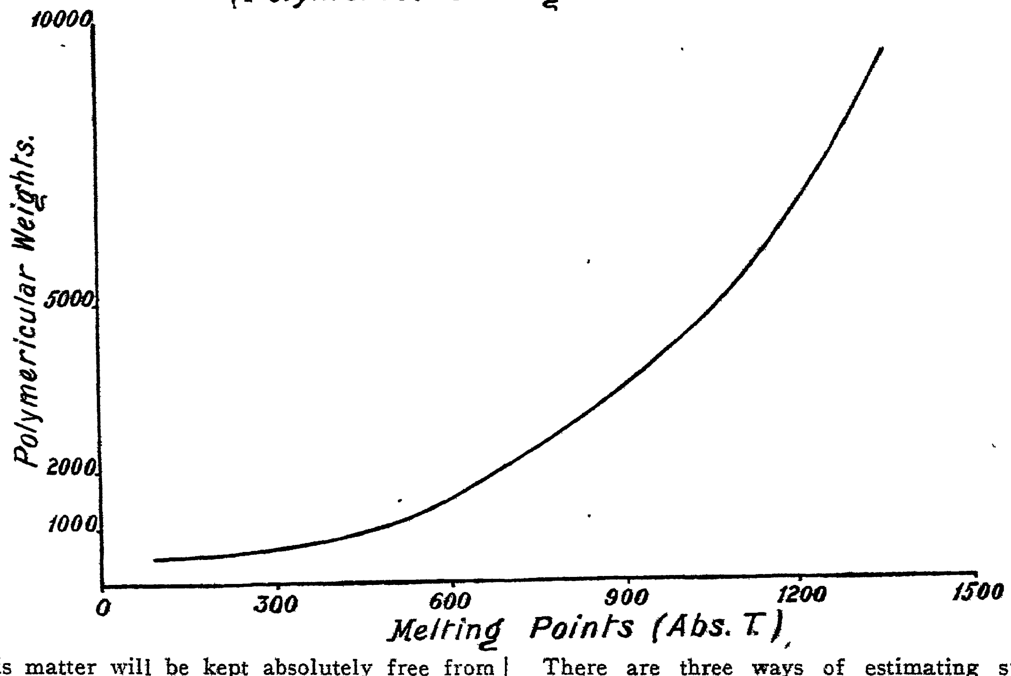
THE present paper is an application of the author's previous results (described in CHEMICAL NEWS, Vol.cxx., No. 3136; Vol. cxxii., No. 3170) to several substances in the neighbourhood of the absolute zero.

Recent work by Kamerlingh Omnes, and Keesom (1915) has provided us with the following specific heats for lead at very low temperatures.

| T | S |
|---|---|
| 46° A. | 0·0242 |
| 22° A. | 0·0143 |
| 14° A. | 0·0075 |

ABSOLUTE ATOMIC WEIGHTS.
(Polymericular Weights at the absolute zero.)




There are three ways of estimating specific heats between 14° and 0° A.

(1) From the specific heats curve the specific heat of lead appears to be zero at about 6° A.

(2) If we plot the above specific heats against absolute temperatures, and produce the curve to 0° A., the following specific heats are obtained :—

| T | S |
|---|---|
| 10° A. | 0·0053 |
| 5° A. | 0·0027 |
| 4° A. | 0·0022 |
| 2° A | 0·0012 |
| 1° A. | 0·00005 |

(3) We can apply Debige's Law (atomic heat=$kT^3$) below 14° A., and get the following values :—

TABLE I. (Lead).

| T | Melticular Weight | R. | $S_T$. | Specific Heats. I | $p$ | II | $p$ | III. | $p$ |
|---|---|---|---|---|---|---|---|---|---|
| 0 | | | | | | | 18 ? | | 3-4000 ? |
| 2 | 1 | 0·0048 | 0·0149 | | | 0·0012 | 12·4 | 0·0000218 | 685 |
| 4 | 3 | 0·0144 | 0·0224 | | | 0·0022 | 10·2 | 0·0001747 | 129 |
| 5 | 4 | 0·0192 | 0·0238 | | | 0·0027 | 8·8 | 0·00034 | 70 |
| 6 | | | | 0·0 | 7·0 | | | | |
| 10 | 8 | 0·0384 | 0·0239 | 0·0053 | 4·5 | 0·0053 | 4·5 | 0·00273 | 8·75 |
| *14 | 12 | 0·058 | 0·0257 | 0·0075 | 3·43 | 0·0075 | 3·43 | 0·0075 | 3·43 |
| *22 | 21 | 0·101 | 0·0285 | 0·0143 | 2 | 0·0143 | 2 | 0·0143 | 2·00 |
| *46 | 51 | 0·245 | 0·0331 | 0·0242 | 1·37 | 0·0242 | 1·37 | 0·0242 | 1·37 |
| *92 | 117 | 0·562 | 0·0380 | 0·0285 | 1·33 | 0·0285 | 1·33 | 0·0285 | 1·33 |

*Specific heats actually observed.

TABLE II. (Water).

| T | Melticular Weight. | R. | $S_T$. | Specific Heats. I | $p$ | II | $p$ | III | $p$ |
|---|---|---|---|---|---|---|---|---|---|
| 0 | | | | | 30 ? | 0·0 | 140 ? | | ? |
| 2 | 1 | 0·166 | 0·516 | | | 0·005 | 103 | 0·000008 | 64500 |
| 4 | 3 | 0·5 | 0·78 | | | 0·01 | 78 | 0·000063 | 12400 |
| 5 | 4 | 0·66 | 0·82 | | | 0·013 | 63 | 0·000125 | 6550 |
| 10 | 8 | 1·33 | 0·827 | | | 0·03 | 27·6 | 0·001 | 827 |
| 20 | 18·5 | 3·08 | 0·958 | | | 0·058 | 16·52 | 0·0077 | 124 |
| *53 | 60 | 10 | 1·232 | 0·146 | 8·44 | 0·146 | 8·44 | 0·146 | 8·44 |
| *140 | 214 | 35·6 | 1·510 | 0·285 | 5·30 | 0·285 | 5·30 | 0·285 | 5·30 |
| *225 | 330 | 55 | 1·529 | 0·463 | 3·30 | 0·463 | 3·30 | 0·463 | 3·30 |
| *273 | 414 | 69 | 1·556 | 0·504 | 3·08 | 0·504 | 3·08 | 0·504 | 3·08 |

TABLE III. (Copper).

| T. | Melticular Weight | R | $S_T$ | Specific Heats I | $p$ | II | $p$ | III | $p$ |
|---|---|---|---|---|---|---|---|---|---|
| 0 | | | | | | | 1200 ? | | |
| 2 | 1 | 0·016 | 0·05 | | | 0·00006 | 833 | 0·000002 | 25000 |
| 5 | 3·8 | 0·06 | 0·07466 | | | 0·00015 | 500 | 0·00003 | 2486 |
| 10 | 8 | 0·127 | 0·079 | | | 0·0004 | 198 | 0·00024 | 330 |
| 12 | | | | 0·0 | 150 ? | | | | |
| *15 | 13·5 | 0·214 | 0·087 | 0·0008 | 109 | 0·0008 | 109 | 0·0008 | 109 |
| *22 | 20·5 | 0·325 | 0·094 | 0·0022 | 42·7 | 0·0022 | 42·7 | 0·0022 | 42·7 |
| *330 | 518 | 8·2 | 0·1545 | 0·0933 | 1·67 | 0·0933 | 1·67 | 0·0933 | 1·67 |

| T | S |
|---|---|
| 10° A. | 0·00273 |
| 5° A. | 0·00034 |
| 4° A. | 0·0001747 |
| 2° A. | 0·0000218 |
| 1° A. | 0·0000027 |

The values of $p$ (degree of polymerisation) calculated from each series of specific heats are widely different (see Table I.).

The serious objection to the third set of results is their magnitude, for between 10—0° A. each lead polymer of ($Pb_8+$) is transformed into a huge one of ($Pb_{3-4000}$)—a miracle of molecular activity! The second result, where $p=18$, appears to be not unlikely.

The results for water are also obtained in the same three ways (see Table II.).

The third set of values seem beyond the reach even of the imagination, and the second set give water a polymericular weight of 140×18=2520 at the absolute zero. The behaviour of other elements, referred to later, makes $p=30$, a more probable value.

The values of $p$ for copper are given in Table III.

The results for carbon (diamond) are obtained in the same way, but are very much larger in magnitude. Thus, the most likely polymericular weights are :—

| | I | II |
|---|---|---|
| Water (m p. 273°) ... ... | 540 | 2520 |
| Lead (m.p. 600°) ... ... | 1456 | 3744 |
| Copper (m.p. 1350°) ... | 9450 | 75600 |

The former values, based on experimental records to almost the absolute zero, are tentatively accepted as correct.

If we plot these values against melting points we obtain (by interpolation) possible values for $p$ for other elements at the absolute zero,

The curve (Fig. I.) is constructed from the following data :—

| T | $p$ | Absolute Molecular Weights (Polymericular Weights) |
|---|---|---|
| Copper (1350°) ... | 150 | 9450 |
| Lead (600°) ... ... | 7 | 1456 |
| Water (273°) ... ... | 30 | 540 |

The curve can be extended in either direction by finding $p$ for other elements of higher or lower melting points.

$p$ has a periodic value as will be seen from the following groups.

GROUP I.

| M.P. | Element | | Polymericular Weight. | $p$ | |
|---|---|---|---|---|---|
| 459 | Li | | 900 | 128 | |
| 371 | Na | | 800 | 35 | |
| 335 | K | | 640 | 16+ | |
| 1356 | | Cu | 9450 | | 150 |
| 311 | Rb | | 600 | 7+ | |
| 1233 | | Ag | 7200 | | 66·6 |
| 299 | Cs | | 560 | 4·2 | |
| — | | — | — | | — |
| — | — | | — | — | |
| 1336 | | Au | 9000 | | 45 |

GROUP V.

| M P. | Element | | Polymericular Weight. | $p$ | |
|---|---|---|---|---|---|
| 63 | | N | 450? | 32+ | |
| 317 | | P | 600 | 19+ | |
| | V | | | | |
| 1123 | | As | 5600 | | 76+ |
| | Nb | | | | |
| 903 | | Sb | 3500 | | 30 |
| | Ps | | | | |
| | | — | | | |
| | Ta | | | | |
| 504 | | Bi | 1180 | | 5·7 |

The transitional elements, arsenic, antimony, and bismuth, thus form a separate sub-group.

GROUP VII.

| M.P. | Element | Polymericular Weight. | $p$ |
|---|---|---|---|
| 50 | F | 450 | 24− |
| 171 | Cl | 500 | 14 |
| 266 | Br | 530 | 6·6 |
| 387 | I | 800 | 6·3 |

$p$ for mercury will only be about 2+ at the absolute zero, whereas argon will be about $Ar_{10}$, and helium still more highly polymerised.

Benzene will be about $(C_6H_6)_7$, naphthalene $(C_{10}H_8)_{5-6}$, and anthracene $(C_{14}H_{10})_{5\cdot5}$. Acetic acid may be $(CH_3COOH)_{10}$.

*Notes.*

(1) If the values of $p$ had been calculated from Debige's specific heats, they would all have been enormously higher.

(2) Certain discrepancies, *e..*, the low value for naphthalene, would disappear on plotting polymericular weights against absolute boiling-points.

(3) The curve would be still more reliable if it were based on the behaviour of, say, half-a-dozen substances.

(4) The numbers of atoms in the benzene, naphthalene, and anthracene polymers at 0° A are about 84, 100, and 132 respectively.

## PRINCIPLES GOVERNING THE GRANT OF MINERAL CONCESSIONS IN INDIA.

By THE HON. SIR THOMAS H. HOLLAND, K.C.S.I., K.C I.E., D.Sc., LL.D, F.R.S.

IT is the business of a mining company to make as much profit as possible out of a mineral deposit during the period of its mining lease: it is the business of Government to safeguard a national asset of vital importance which cannot be replaced or renewed. But it is better for a country that its mineral deposits should be worked than that they should be left lying idle in the ground. The problem before Government, therefore, or before any large owner of mineral rights, is to frame conditions for the grant of mineral concessions which will ensure a fair return to the State, without undue waste, and yet be liberal enough to attract the investor in mines.

The mineral policy of a Government is thus the choice of a judicious mean between extravagance and conservatism. And as the values of minerals vary with the industrial development of a country and that of the countries with which it is in trade communication, this judicous mean wll gradually shift its position between the two extremes. Yet, to attract the investor, stability of policy is also necessary; and thus, whilst the rules for the grant of mineral concessions should be modified from time to time to safeguard the interests of theState, frequent changes which will unsettle private enterprise must be avoided.

In a country as large as India, a mineral that is workable in one province may be unworkable in another, where fuel may be scarce, means of transport undeveloped, or markets unobtainable. Thus, some local variations in the conditions for the grant of mineral concessions may be necessary; yet, because the development of one mineral is often not possible without the simultaneous development of another, the rules should prescribe limiting conditions sufficiently narrow to ensure a judicious degree of uniformity over wide areas.

The whole problem of framing and workng a mineral policy for all India is, thus, the choice of a judicious mean in all things—rents, royalties, terms, areas, and conditions of tenure.

As justification for *conservatism*, the Government has to realise:—

(1) That mineral products are essential for the maintenance of modern civilised activities; when they approach exhauston, the country will be absolutely dependent on foreign sources.

(2) That a mineral once worked is lost to the country for ever: nothing can renew a mineral deposit.

(3) That the miner works only those parts of the deposit that are commercially profitable at the time, often leaving behind far larger quantities of the same mineral in a condition even less fitted than before for profitable exploitation; a mineral deposit which is not worth working to-day may become of great value when processes are improved, or when, through industrial development, local markets become changed.

(4) That, when a company obtains a mining lease, the State, as the owner of mineral rights, goes into effective partnership with the company. The State contributes the mineral deposit as its share of the capital, whilst the mining company provides the working capital. At the end of the lease, when the mineral deposit has been worked out, the State's share of the capital has disappeared, whilst the mining company has secured the profits, and, if successful, has redeemed the whole of its investment. A mineral deposit, therefore, becomes a wasting State asset from the date on which it is leased to an active mining company, and the only compensation that the State obtains for the exhaustion of its mineral deposits

is (*a*) the royalty paid, and (*b*) the money spent in local work. As the royalty rates now prescribed in India are rarely more than one-fortieth of the actual mineral values, the return to the State under present conditions is less than the potential value of the mineral; for the royalty is paid on the mineral actually sold by the miner, and not on that left behind through his bad working, or because, at the time, the deposits are locally too poor to be worth exploitation.

The whole process of mineral exploitation is, thus, essentially wasteful: large quantities of rich mineral are left behind for various reasons; larger quantities are damaged by disturbance of the ground in mining; a large percentage of each mineral is lost during the process of dressing for the market or the smelter; and, in the case of ores, a serious percentage is lost in the process of smelting. Finally, the refined product is used in the Arts, and thus scattered too widely to make it payable to collect again into workable form. A workable mineral deposit is the product of natural processes of concentration which have been going on for geological ages; but the results of these slow processes are undone in a few years by the miner, whose every mistake is irreparable. It has been well said that, whilst the results of bad farming can be recovered and the fertility of damaged land can be renewed, there are no fertilisers for worked-out mines.

As justification, on the other hand, for *liberality*, it is necessary to remember:—

(1) That most mining enterprises are highly speculative, and the investor wants the encouragement of generous terms before he will risk his capital in an unproved country.

(2) That most of the capital is sunk in an irrecoverable form: the miner cannot sell underground galleries and shafts in the open market; he must, therefore, hope to recover his capital outlay from profits and that in a relatively short period.

(3) That, unless a miner can now and then reap the benefit of an occasional windfall, he will not be justified in writing off the losses due to the large number of unlucky ventures which seem to be the constant accompaniments of mining enterprises.

(4) That mineral products are essential to most industries, and it is much better to use them even wastefully than to leave so much national capital lying idle.—*Journal of Indian Industries and Labour*, May, 1921.

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THE June and July issue of the *Journal of the Franklin Institute* contains a paper that was presented at the Annual Meeting of the Institute held in January, by John E. Lieb, M.E., detailing the remarkable discoveries and experiments of Leonardo da Vinci in engineering. The article is very fully illustrated. The multiplicity of devices is remarkable, and include a cyclometer, a pedometer, a dynamometer, a spring-driven automobile, a friction-driven fire escape, and wings for a flying machine. Numerous extracts from his diary show that he lived much in advance of his time, and many of his devices are of present-day interest.

## FUEL PROBLEMS OF THE FUTURE.*

By SIR GEORGE T. BEILBY, F.R.S.

TURNING now to oil, the other great natural source of fuel, we find that the world's output for 1920 was about 97 million tons, of which the

| | Per cent |
|---|---|
| United States produced ... | 64·8 |
| Mexico ... .. .. .. ... | 23·3 |
| Russia ... .. .. ... | 3·5 |
| Dutch East Indies ... ... | 2·5 |
| India ... ... ... ... ... | 1·2 |
| Roumania ... ... ... | 1·1 |
| Persia ... ... .. ... | 1·0 |
| Countries producing less than 5 per cent ... ... | 2·6 |
| | 100·0 |

The oil output therefore amounted to 7 per cent of the fuel output of the world, reckoned in tons If reckoned in potential therms, the figure would be raised to 10 per cent.

As the United States has extensive oil interests in Mexico, it may be taken that last year she controlled 75 to 80 per cent of the total output of the world. It is therefore significant that, in official quarters, grave anxiety has been expressed as to the probable exhaustion of these resources in view of the rapid development in the use of motor spirit for road transport and of fuel oil for transport by sea.

While we are justified in discounting to some extent the elements of popular panic which have been obvious in much that has appeared in technical journals, as well as in the daily Press, the fact remains that, but for the rapid development of production in Mexico, and the extensive interests of the United States in this production, the actual danger of shortage in America would have already become more acute.

The following extract from a statement by Mr. J. O. Lewis, Chief Petroleum Technologist to the United States Bureau of Mines, expresses so very clearly the American view of the oil problem of the future that I cannot do better than quote it *in extenso*. No mere paraphrase would convey the same impression of reality.

"The United States Geological Survey during the last ten years has made several estimates of the quantity of oil left in our old fields. The most recent estimate—that of David White—indicates that about 40 per cent of the oil had been brought to the surface, and that the 60 per cent remaining underground, if recovery as needed were possible, would last barely 20 years at the present rate of consumption. As the period in which an oil field can be made to yield its oil is not wholly within the control of man, the domestic production will undoubtedly be spread over a much longer period than that estimated; but, on the other hand, the peak of production will be passed long before 20 years, and thereafter production will be at a declining rate Of course, such estimates are by no means infallible, as many obscure factors are involved. However, this statement represents the opinion of the agency best qualified to make such an estimate, and is indicative of a condition which, were there no other solution to the problem, would be highly unsatisfactory,

*Delivered in the theatre of the Institution of Civil Engineers, London. Inserted by favour of the *Gas Journal*, June 29, 1921.

and would be viewed by the automotive industry with the greatest concern. For, even were the estimate unduly pessimistic, and the actual reserve twice that shown, the condition would still be unsatisfactory.

The preceding statement refers only to the oil from oil wells in the United States. Fortunately there are enormous undeveloped resources in the rest of the world. The petroleum resources of this country have been developed and depleted in a ratio far beyond that of other countries, so that although we are producing to-day two-thirds of the world's production, the opportunities elsewhere for increasing production are much greater than in the United States. Geologists and those well informed on foreign resources believe that in all probability the world contains enormous reserves of oil that can be obtained upon demand. Although to obtain oil from these reserves may not be as satisfactory as to obtain it within the confines of the United States, the outlook tends to assure the future of the internal combustion engine.

Fortunately, oil may be obtained from other sources than oil fields. In various parts of the United States, particularly in Colorado, Wyoming, and Utah, are enormous bodies of oil shales from which oil may be obtained by destructive distillation, as benzole is obtained from coal. The United States Geological Survey has estimated the quantity of oil locked up in the richer shales of the three States mentioned as perhaps ten times the amount of the oil reserve in the oil-fields. In Scotland, the retorting of oil from oil shales has been on a commercial basis for more than 50 years, and antedates the oil industry in the United States. Commercial and semi-commercial experiments are being made in order to determine whether the oil shales of the Western States can be mined and retorted profitably in competition with petroleum from oil fields. This problem has not yet been solved; but these shales constitute a latent reserve that protects the future needs of the country for motor fuel as far as these needs can be foreseen. However, oil cannot be obtained from the shales on a large scale without heavy investments; and the development of the industry must be spread over many years. Also, when that time comes, the consumer will probably have to pay more for his gasoline.

As regards the question of substitutes, if prices of petroleum products advance sufficiently, alcohol may become one of the motor fuels of the future. The efficient use of alcohol requires, however, certain modifications in the present design of the mobile internal combustion motor. Moreover, large quantities of lubricants are required, in addition to motor fuel. Hence it seems desirable to continue to depend on crude oil as a principal source as long as possible, especially as crude oil is the only known satisfactory raw material yielding both motor fuel and lubricants.

Briefly, motor fuels may be obtained from four possible sources: (1) Petroleum from our own wells; (2) petroleum from wells in foreign countries; (3) oil from our oil shales; (4) gasoline substitutes. As to the first, there is serious but not immediate concern. As to the second, it is believed that there remain enormous potential reserves outside the United States. As to the third, there are known deposits of oil shales which, in three States alone, promise to yield many times more oil than will be ever be recovered from our oil wells. As to the fourth, it is probable that eventually alcohol could meet our needs should gasoline fail. Thus, while there is concern over our own domestic supplies of petroleum from oil wells, there is no concern as to the ultimate supply. There may be critical periods when one source fails, and before another has been developed; also it is not unlikely that when our own wells fail, and we have to fall back on oil from foreign coutries or oil shales, we shall have to pay more for our motor fuel.

In view of this reference to alcohol as a probable substitute for motor spirit, it may be well here to refer to the action of the British Government in this connection.

In view of the national importance of the subject, Mr. Walter Long appointed a Committee in October, 1918, to report upon:

(1) The various available sources of supply of alcohol, the methods of manufacture, and the cost of the product.

(2) The suitability of alcohol, either alone in admixture with solid, liquid, or gaseous combustible substances, for use in internal combustion engines, and the modifications of the existing types of such engines which may be necessary to the attainment of efficiency.

(3) The question of denaturing the alcohol, and the alterations to be made in the present Excise Bill.

The Committee obtained much useful information of a preliminary nature; and in June, 1919, they issued a report which was presented to Parliament on June 30.

One of the recommendations of the report was: "That an organisation should be established by the Government to initiate and supervise experimental and practical development work, at home and overseas, on the production and utilisation of power alcohol, and to report from time to time for public information on all scientific, technical, and economic problems connected therewith."

This report was in due course considered by the Committee of Council for Scientific and Industrial Research, who recommended the Fuel Research Board to continue the investigation of the problems.

As a first step in these inquiries, the Fuel Research Board recommended the appointment of Sir Frederick Nathan as Power Alcohol Investigation Officer. This appointment was confirmed by the Lord President on December 17, 1919. Since his appointment, Sir Frederic Nathan has devoted his whole time to these inquiries, and has been in close touch with the Government Departments interested in the questions involved.

In July, 1920, an Interim Memorandum on "Fuel for Motor Transport" was published by the Fuel Research Board, in which the situation at that date was summed up as follows:—

"The main sources of alcohol are vegetable materials containing starch or sugar; and practically all the alcohol for potable and industrial purposes is now made from grains or molasses. Before the war, large quantities of alcohol were made in Germany from potatoes, specially grown for the purpose.

Alcohol can also be produced from the ferment-

| | Quantities. Required for 250 Million Gallons Tons. | United Kingdom Production, 1919 Tons | Acreage.* Required for 250 Million Gallons.† | Under Crop in 1919 | Raw Material. Average Price per Ton, 1919, £ s. d | Cost per Gallon of Alcohol: s. d. |
|---|---|---|---|---|---|---|
| Grain (barley) | 4,170,000 | 1,288,035 | 5,593,293 | 1,870,087 | 21 4 0 | 7 0 |
| Potatoes | 12,500,000 | 6,312,000 | 2,118,644 | 1,218,774 | 8 10 6 | 8 6 |
| Mangolds | 25,000,000 | 7,769,000 | 1,282,513 | 471,759 | 1 10 0 | 3 0 |

* Total arable acreage of the United Kingdom—about 21 million acres
† Based on ten years' average yields

able sugars formed by the hydrolysis of wood cellulose, and synthetically from calcium carbide, or from the ethylene contained in coke-oven and coal gas. The quantity of waste wood in this country for alcohol production is, however, negligible. Calcium carbide is impossible, as it cannot be produced in quantity without cheap power; and the recovery of ethylene from coke-oven and coal gas, and its conversion into alcohol, are still in the experimental stage. At the present time, therefore, none of these three sources of supply is of appreciable commercial importance in this country.

The vegetable materials growable in this country from which alcohol could be made are grain (barley), potatoes, and mangolds; and the following figures relating to the production of 250 million gallons of 95 per cent alcohol are interesting (see Table above).

These figures are not encouraging; and generally it may be stated that the production of alcohol in any considerable quantities from vegetable materials grown in the United Kingdom is not economically possible owing to: (1) Insufficient acreage; (2) the high cost of cultivation and harvesting; (3) the high cost of manufacture; and (4) the fact that the most suitable raw materials are also important foodstuffs. There is for these reasons no prospect of replacing any considerable quantity of petrol by home-produced alcohol. Moreover, it is unthinkable that land, for even a fraction of the quantity of the raw materials in the above Table, could be used for such a purpose, when in the matter of food production, a week-end supply only is assured from our own land.

(To be continued).

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. clxxiii., No. 4.

"Critical Potentials and Band Spectra of Nitrogen."—By MM. Léon and Eugène Bloch.

"The Conductivity of a Solution of Euprammonium Citrate compared with that of Copper Sulphate"—By MM. F Beaulard de Lenaizin and L. Maury.

"Flocculation of Colloidal Arsenic Sulphide Influence of the Dilution of the Electrolyte and of the Quantity of the Electrolyte."—By MM. A Boutaric and M. Vuillaume.

"Compounds of the Halogen Derivatives of Mercury and Thallium."—By MM. J. Barlot and Penot.

"Sulphonations in Presence of Iodine."—By M. V. Auger and Mddle. M. Vary.

## NOTES.

Institute of Metals.—The following is the Programme of the more important arrangements at the Autumn Meeting, Birmingham, September 21 to 23, 1921.

Tuesday, September 20—The Office of the Hon. Local Secretary (Mr. G. W. Mullins, M.B.E.), will be open at the Municipal Technical School, Suffolk Street, Birmingham, for the issue of tickets, badges, &c., and for general information.

Wednesday, September 21.—General Meeting of Members in the Examination Hall, Municipal Technical School, Suffolk Street, by kind permission of Dr. W. E. Sumpner, Principal. The Lord Mayor of Birmingham, Alderman William A. Cadbury, will open the Meeting with a brief address of welcome. Papers will be presented and discussed. Members assemble at the Grosvenor Rooms, Grand Hotel, Colmore Row, for Luncheon, by kind invitation of the Metal Trades' Association, viz., Brass and Copper Tube, Brass Wire, Brassfounders Employers', Brazed Brass Tube, British Aluminium Hollowware Manufacturers', Cold Rolled Brass and Copper, and Nickel Silver Associations. Visit to the University. Reception by the Vice-Chancellor of the University (Sir Gilbert Barling, Bart., C.B., C.B.E.) in the Great Hall; Address by the Principal (C. Grant Robertson, Esq., C.V.O., M.A.). Civic Reception by the Lord Mayor (Alderman W. A. Cadbury) in the City Art Gallery.

Thursday, September 22.—General Meeting of Members. Papers will be presented and discussed as time permits. Members meet at tram termini or railway stations (as per Local Reception Committee's later programme) for visits to works Reception for Garden Party at the Botanical Gardens, Edgbaston.

Friday, September 23.—Motor Excursion to Kenilworth, Warwick, and Stratford.

In view of an expected considerable accession of new members in connection with the Birmingham Meeting, a Special Council Meeting is being held in London on September 7, for the purpose of considering Applications for Membership. All applicants for membership whose forms are in the Secretary's hands before noon on September 7 will be entitled to take part in the proceedings in connection with the Birmingham Meeting. Members

are asked by the Council to be good enough to convey this information to any of their friends who may be eligible for membership of the Institute, or send the addresses of such friends to the Secretary. The new List of Members is available upon request being made. A large number of papers are promised, and we hope to publish abstracts as soon as they have been read. Visits have been arranged to the following works: Alldays & Onions, Small Heath; W. & T. Avery, Ltd., Soho Works; Belliss & Morcom, Ltd., Ladywood; Birmingham Small Arms Co. Ltd., Small Heath; Cadbury Bros., Bournville; Earle, Bourne & Co., Ltd., Heath Street South; Elkington & Co., Ltd., Newhall Street; Elliott's Metal Co. Ltd., Selly Oak; Allen Everitt & Sons, Ltd., Smethwick; Kynoch, Ltd., Witton; Metropolitan Carriage, Wagon and Finance Co. Ltd, Saltley; Muntz's Metal Co. Ltd., French Walls; Tangye's, Ltd., Cornwall Works; H. Wiggin & Co. Ltd., Wiggin Street; Wolseley Motors, Ltd., Adderley Park.

CITY AND GUILDS OF LONDON INSTITUTE.—Mr. H. P. Philpot, B. Sc., A.M.Inst C.E., Assistant Professor at University College, has been appointed to the Professorship of Civil and Mechanical Engineering at the Finsbury Technical College; and Mr. A. J. Hale, B.Sc., F.I.C, Chief Assistant in the Department of Applied Chemistry to the Professorship in that Department. The entrance examination of the College will be held on Tuesday, September 20.

WE learn from the *Board of Trade Journal* that a notice has been issued by the East Prussian State Railways advising precautions against pilferage. It is stated that binding packing cases with band iron is valueless unless special precautions are taken, and it is advised that cases should be first nailed together and then bound with iron; minute instructions are given as to how the iron should be nailed on to prevent theft.

TREATMENT OF CRUDE POTASSIUM SALTS.—In an article which appeared in *Kali*, No. 3, 1921, the writer, Mr. O. Krull, dealing with the manufacture of potassium chloride, describes the *modus operandi* which enabled him to determine the solubility and speed of dissolution of chlorides of sodium and potassium, both separately and mixed. He then applies the data found to the industrial treatment of sylvinite, and notes that regularity in the composition of sylvinite is the most important factor for satisfactory manufacture of potassium chloride.

THE BROMINE INDUSTRY.—The bromine industry, almost entirely German and American before the war, had acquired a very considerable development, and is an industry deserving of note. The raw material is the mother-water from manufacture of potassium salts at Stassfurt, which contain 3 to 5 grms. of bromine in form of magnesium bromide. This water, heated to 80° C., is conveyed to the top of a tower lined with refractory materials. A mixture of steam and chlorine enters at the base, and the gaseous bromine escapes at the top to be condensed in a stone-ware worm The bromine obtained yet contains 2·5 per cent chlorine, and must be rectified on iron bromide. Kubierschky invented an apparatus constructed on the same principles, but with a plate column, thus obtaining good anhydrous bromine, with recovery of heat from the spent mother-water and continuous rectification of the bromine in a second plate apparatus. Thus almost chemically pure bromine can be directly produced, and the entrained chlorine, escaping in a gaseous form and returning to the base of the first column, recovered.—*Industrie Chimique*, May, 1921.

## NEW COMPANIES.

The under-mentioned particulars of New Companies recently registered are taken from the Daily Register compiled by JORDAN & SONS, LIMITED, Company Registration Agents, Chancery Lane, W.C.2.

DYMOND TAR CHEMICALS & FUELS, LIMITED.—(176029)—Registered July 29th, 1921. Headlands Works, Liversedge To carry on the business of Tar and Chemical Manufacturers. Nominal Capital: £30,000 in 30,000 Shares of £1 each. Directors. H. P. Hird, Moor End House, Dewsbury Moor, Dewsbury; F. D. Richmond, Lower Popeley, Liversedge; J. Haigh, Scout Hill, Dewsbury, W. Glossop, Highfield, Hipperholme, H. A. Glover, Morley, Hipperholme; C. S Hays, Vermont Villa, Liversedge, R. Yielding, Birstall Qualification of Directors. 100 Shares. Remuneration of Directors. To be voted by Company.

NORMAN V. STOW, LIMITED.—(176042)—Registered July 29th, 1921. To acquire and carry on the business of Chemists, Druggists, Oil and Colourmen. Nominal Capital: £3,500 in 3,500 Ordinary Shares of £1 each. Directors: N. V. Stow, Belfield, Forde Park, Newton Abbot, G. B Purser, 15, Abbotsbury Road, Newton Abbot (Managing Director); A. Sampson, 2, Devon Square, Newton Abbot, R. Cubitt, Clinton House, Ashburton. Qualification of Directors: £100 Managing Director: £1,000. Remuneration of Directors To be voted by Company in General Meeting.

THOMAS ASPINALL, LIMITED.—(176048)—Registered July 29th, 1921. 6, 8 & 10, Bank Street, Bolton. To acquire and carry on the business of Manufacturing, Wholesale and General Chemists Nominal Capital £5,000 in 5,000 Shares of £1 each. Directors. T. Aspinall, 48, Somerset Road, Bolton, F. A. Lowe, 32, Harpers Lane, Bolton. Qualification of Directors. £100. Remuneration of Directors. To be voted by Company.

ARTHOL MANUFACTURING COMPANY, LIMITED.—(176051)—Registered July 30th, 1921. To acquire and carry on the business of Manufacturers of Synthetic Perfumes and Essential Oils of all kinds. Nominal Capital: £25,000 in 25,000 Ordinary Shares of £1 each. Directors. J. F. Barvoets, 20, Deane Road, Liverpool; R. F. Morris, Rose Bank, Wilmslow, Cheshire (Managing Directors). Qualification of Directors: One-fourth of the issued capital. Remuneration of Directors To be voted by Company in General Meeting.

MC INNES COMPOSITIONS COMPANY (1921), LIMITED.—176071—Registered August 2nd, 1921. To acquire and carry on the business of Anti-corrosive and Anti-fouling Compositions and Paint Manufacturers and Merchants. Nominal Capital £50,000 in 40,000 Participating Preference Shares of £1 each and 40,000 Ordinary Shares of 5/- each. Directors: To be appointed by Subscribers. Qualification of Directors: 1 Share. Remuneration of Directors: £100 each. Subscribers. F. M. B. Fisher, 4, Cullum Street, E.C.3.; G N. Reeves, 7, East India Avenue, E.C.3.

CARTLIDGE BROTHERS, LIMITED.—(176054)—Registered July 30th, 1921. 36a, Darlington Street, Wolverhampton. To carry on the business of Oil Merchants and Refiners. Nominal Capital: £5,000 in 1,000 Preference Shares and 4,000 Ordinary Shares of £1 each. Directors: J H. Cartlidge, Mount Road, Penn, Near Wolverhampton; L. Cartlidge, Park Side, Etruria Road, Basford, Stoke-on-Trent. Qualification of Directors: £250. Remuneration of Directors. £100 each.

## New Patents.

THIS LIST is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W.C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

20331—Cumberland Coal Power & Chemicals, Ltd.—Production of solid products from ammonia gas. July 28.

20258—Dutt, E E.—Extraction of titanium dioxide and alumina from titaniferous bauxite. July 28.
20258—Godfrey, S. H.—Extraction of titanium dioxide and alumina from titaniferous bauxite. July 28.
20417—Green, A. G.—Process for manufacture of phthalimide. July 29.

*Specifications published this Week.*

143850—Norsk Hydro-Elektrisk Kvaelstof-Aktieselskab.—Process for the production of formate of ammonium from barium cyanide.
166767—Dreyfus, H.—Manufacture of cellulose derivatives.
145696—Collin Akt Ges. ver Verwertung von Brennstoffen und Metallen, F. J.—Process of producing ammonium sulphate from cyanogen compounds produced in the distillation of coal or organic substances.

*Abstract Published this Week.*

*Sulphuric Acid.*—Patent No. 164572.—Mr R. F. Dior, of 18, Rue du Dome, Billancourt, France, has obtained a Patent for an improved apparatus for obtaining sulphuric acid. In a series of sulphuric acid chambers, their size and height decrease in order, the tallest being connected with the Glover, and the shortest with the Gay Lussac tower. Each resembles in shape an inverted funnel, in which the sides of the upper part are more vertical than the sides of the lower part. The gases, which enter at the bottom and leave at the top, are caused to move spirally by placing the inlet and outlet respectively, tangentially to the circumference of the chamber. In order to control the flow of the gases, a vertical shaft placed in the centre of the chamber may be employed. For the same purpose, jets of steam, atomized water, or dilute sulphuric acid may be directed in a downward direction by injectors from the top of the chamber or from the sides. Sulphuric acid of about 53°, is poured continuously down the inner surface of the chamber by means of the annular groove and cap or by any other device such as the turbine. The outer walls are kept cool by means of cold water which flows from the trough and is collected. When four of such chambers are connected in series, the dilute acid produced in the second is used to supply the first, and that produced in the third and fourth is conveyed to the top of the second. The strong acid formed in the first chamber is partly removed from the system and the remainder is led to the third and fourth chambers. In this way the dilute acids are concentrated in the first two chambers and the nitrous gases recovered to some extent, in the last two chambers, thereby assisting the working of both the Glover and Gay Lussac towers.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

# NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemical Apparatus, &c., for review or notice to be addressed to the EDITOR.

**SUBSCRIPTIONS**, £1 12s. per annum, payable in advance, should be addressed to the MANAGER.

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# THE CHEMICAL NEWS.

VOL. CXXIII., No. 3202.

## BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

THE 69th Annual Meeting of the British Association will be held in Edinburgh from Wednesday, September 7 to Wednesday, September 14.

The Inaugural General Meeting will be held in the Usher Hall, on Wednesday, September 7, at 8.30 p.m., when Sir Edward Thorpe, C.B., F.R.S., will assume the Presidency in succession to Professor W. A. Herdman, C.B.E., F.R.S., and will deliver an Address dealing with "Some Aspects and Problems of Post-War Science, pure and applied."

On Friday, September 9, at 8.30 p.m., in the Usher Hall, the First Evening Discourse will be delivered by Professor C. E. Inglis, O.B.E., M.A., on "A Comparison of the Forth and Quebec Bridges, showing the Evolution of Cantilever Bridge Construction during the past Thirty Years."

On Tuesday, September 13, at 8.30 p.m., in the Usher Hall, the Second Evening Discourse will be delivered by Professor W. A. Herdman, C.B.E., F.R.S., on "Edinburgh and Oceanography."

The Concluding General Meeting will be held on Wednesday, September 14, at 12 noon.

At the Inaugural Meeting, Members of the General Committee may occupy the raised seats on the platform. In the area a few rows only will be required for official use. At the Evening Discourses, a limited number of seats on one side of the hall only will be retained for the General Committee and official use. To all other seats, the whole of which command uninterrupted view and hearing, the Membership Ticket will admit, without further ticket.

Four Public Lectures to Citizens will be given by Members of the Association in connection with the Meeting.

On Tuesday evening, September 6, at 8 p.m., in the Usher Hall.—Sir Oliver J. Lodge, F.R.S., on "Speech through the Ether, or the Scientific Principles underlying Wireless Telephony."

On Wednesday afternoon, September 7, at 2.30 p.m., in the Natural History Theatre, Old College University.—E. J. Russell, D.Sc., F.R.S. (special lecture, arranged in collaboration with Section M, Agriculture, on behalf of agricultural interests in Edinburgh and neighbourhood), on "Science and Crop Production."

On Thursday evening, September 8, at 8 p.m., in the Usher Hall.—Professor A. Dendy, D.Sc., F.R.S., on "The Stream of Life."

On Monday evening, September 12, at 8 p.m., in the Usher Hall.—Professor. H. J. Fleure, D.Sc., on "Countries as Personalities."

Arrangements for these Lectures are in the hands of the Local Executive Committee, in collaboration with the local branch of the Workers' Educaitonal Association.

Sectional Addresses.—The following Addresses will be given by Sectional Presidents. These Addresses will be distributed throughout the programme, and those marked * will be introductory to discussions :—

A—Problem of Physics. By Prof. O. W. Richardson, F.R.S.

B—The Laboratory of the Living Organism. By Dr. M. O. Forster, F.R.S.

C—Experimental Geology. By Dr. J. S. Flett, F.R.S.

D—Some Problems in Evolution. By Prof. E. S. Goodrich, F.R.S.

E—The Application of Geography. By Dr. D. G. Hogarth, C.M.G.

F—The Principles by which Wages are Determined. By W. L. Hichens, Esq.

G—Water Power. By Prof. A. H. Gibson, D.Sc.

I—The Boundaries of Physiology.* By Sir W. M. Fletcher, K.B.E., F.R.S.

J—Consciousness and the Unconscious.* By Prof. C. Lloyd Morgan, F.R.S.

K—The Present Position of the Theory of Descent, in Relation to the Early History of Plants.* By Dr. D. H. Scott, F.R.S.

L—The Place of Music in a Liberal Education.* By Sir Henry Hadow, C.B.E.

The following subjects (among others) will be discussed at joint meetings of the Sections indicated: The Structure of Molecules (Sections A, B). The Age of the Earth (Sections A, C, D, K). Biochemistry (Sections B, I). The Proposed Mid-Scotland Canal (Sections C, G). The Origin of the Scottish People (Sections E, H). Vocational Training and Tests (Sections F, J, L). The Relation of Genetics to Agriculture (Sections D, K, M).

Papers read at the meeting will be published in the CHEMICAL NEWS with as little delay as possible.

## THE COLOUR OF THE LIGHT FROM THE NIGHT SKY.*

By LORD RAYLEIGH, F.R.S.

THE general light of the sky at night is very faint, and beyond the observations of Campbell (*Astr. Soc. Pacific*, 1917, xxix., 218) and Slipher (*Astr. Jour.*, 1919, xlix., 266), who could always detect the aurora spectrum line in temperate latitudes, nothing appears to be known of its spectroscopic or chromatic character. Slipher, indeed, suggested that the variability in its brightness recorded by Yntema might be accounted for by attributing the light mainly to a variable aurora. But this view has been controverted, rightly as I think, by Fabry (*Astr. Jour.*, 1919, l., 308). My own observations, now to be recorded, indicate that at the time and place where I was working, little, if any, of the light could be attributed to the green aurora line.

The great difficulty of spectroscopic observations is, of course, the want of light; though if the light were monochromatic, as, for instance, if it were all concentrated in the aurora line, this difficulty would be much mitigated. I thought it worth while, however, to try if anything could be learnt by a cruder method, which possesses some advantages even if the light is not very feeble.

*Reprinted by permission from the *Proceedings of the Royal Society*, A. Vol. xcix.

A series of small coloured filters were arranged so as each to transmit a limited portion of the spectrum. These were placed in a suitable frame, which held in addition a neutral-tinted photometric wedge of carbon in gelatine, made by Mr. Sanger-Shepherd. This wedge was graduated in equal parts, according to Hunter and Driffield's method. (Scale-reading 10, light transmitted = 1/10; scale reading 20, light transmitted = 1/100). A photographic plate was placed in the frame, so that part of it was under the various colour filters, and another part under the wedge. This could be exposed to the night sky or other source of light.

After development, the photographic intensity under each coloured screen will match the intensity under some point on the wedge. The plate, therefore, gives a record of what fraction of the total photographic effect due to the source is transmitted by each screen. For comparable results with different sources of light, it is of course necessary to keep to the same kind of photographic plate.

The great advantage of the method is that it allows light to be used from a cone of very large angular aperture. With a spectroscope we cannot, under the most favourable circumstance, use an aperture ratio of more than 1 : 2. But a plate under the coloured filters may be exposed to the entire hemisphere if desired. Moreover, when faint impressions are concerned, a large patch of defined shape and uniform, even if small, intensity practically gives much more confidence to the experimenter than a small and faint spectrum. The information given is, of course, of a rather different kind.

Coming now to details. The coloured screens were :—

| | Transmission. |
|---|---|
| 1. Ultra-violet glass, supplied by Messrs. Chance ... ... ... ... | 3300-3800 |
| 2. Cobalt blue glass. Several thicknesses ... ... ... ... ... ... | 4000-4500 |
| 3. Bluish-green glass ... ... ... ... | 4300-5300 |
| 4. Green glass ... ... ... ... ... | 5100-5900 |
| 5. Flavazine ... ... ... ... ... | 5500-7000 |
| 6. Flavazine, with didymium glass | 5500-5630 and 5930-7000 |
| 7. Wratten's red filter, No. 23A ... ... | 5800-7000 |

These were chosen, so far as possible, to give nearly the same photographic density with sunlight. This is desirable, because the range of intensities which the plate can deal with is not unlimited. The green and red filters, which transmit portions of the spectrum to which the plate is comparatively insensitive, were chosen to give as large transmission as was consistent with isolating a fairly narrow range of the spectrum.

Filter No. 6 was designed to isolate as nearly as possible the green aurora line, if present. No filter could be found to cut out the red without at the same time involving serious loss of green.

Ilford special rapid panchromatic plates were used. These were far more effective in the red, yellow, and green regions than any other plates I have tried. All the results recorded were obtained with a consignment of plates bearing the same number, and therefore, presumably, as nearly alike as may be.

An ink mark on the under face of the wedge gave a fiducial mark on the negative, and starting from this, the wedge scale was copied by hand on to the developed film, marking it on with a fine pen.

The photometric work on the developed plates was done with the photoelectric apparatus described in connection with the scattering of light by gases (*Proc. Roy. Soc.*, 1920, xcvii., 440). Briefly, it depends on a photoelectric cell with battery and galvanometer. The plate rests on a table, in which is a slit. Above is a bright light focussed on the slit with a lens. The rays diverging beyond the focus fall on the photo-electric cell. The deflection of the galvanometer depends on the opacity of the photographic film. The impression through a colour filter was placed on the slit, film downwards, and the deflection noted. The impression of the wedge was then substituted, with the length of the slit at right angles to the length of the wedge. The plate was then slid along until the previous deflection was recovered, and the postion of the slit on the wedge scale noted.

On a given negative, the result was usually recovered to within about 0·2 of a scale division, but, with another negative, discrepancies as large as 1 scale division (representing a factor of 1·26), or even more, were observed. These are due either to inequalities in the photographic film or to changes in the quality of light received from the source, due to varying atmospheric conditions (see the remarks in my paper, *loc. cit.*, p. 442 The plates used in the present work were coated on common glass, not plate glass).

The photoelectric measurement of a given negative was very satisfactory, and far preferable to visual photometry. (The latter can, no doubt be applied to smaller areas on the negative, which is important in some investigations).

The first series of experiments was made with the plate exposed to the entire sky, so far as it was not blocked out by trees and buildings. This method is open to the objection that some of the rays pass very obliquely through the coloured screens, with the result that the effective thickness of the latter becomes somewhat indefinite. This however, does not seem to vitiate the result appreciably, as subsequent experience showed; while an important advantage is gained in shortening the exposure.

Comparison of the night sky with the clear twilight sky (Table I.) shows clearly how much poorer the latter is in yellow and red light. The wedge readings for the two yellow and the red filter differ by about 4 scale divisions, showing that, for the night sky, the yellow and red components account for 2·5 times as large a percentage of the whole photographic effect as in the twilight sky.

TABLE I.

The Figures given are the Wedge Readings, obtained as described.

| | Starlight sky. Aug. 9. | Starlight sky. Sept. 6-7. | Twilight, clear sky. Aug. 17. |
|---|---|---|---|
| Ultra-violet glass ... | 10·6 | 10·0 | 9·9 |
| Cobalt glass ... ... ... | 13·1 | 13·3 | 12·4 |
| Bluish-green ... ... | 12·5 | 12·2 | 11·3 |
| Green ... ... ... ... | 14·7 | 13·7 | 16·1 |
| Flavazine ... ... ... | 8·5 | 8·0 | 13·1 |
| Flavazine with didymium | 12·1 | 10·9 | 16·1 |
| Red ... ... ... ... ... | 10·7 | 10·0 | 15·0 |

TABLE II.

| | Starlight sky. Sept 15-16. | Starlight sky. Oct. 8, 9, 10. | Starlight sky. Mean. | Blue sky at sunset. Sept. 27. | Blue sky at sunset. Sept. 28. | Blue sky. Sept. 24, 1 p.m. |
|---|---|---|---|---|---|---|
| Ultra-violet glass | 13·2 | 11·9 | 12·6 | 12·3 | 15·4 | 10·4 |
| Cobalt glass | 14·9 | 14·8 | 14·8 | 13·5 | 12·8 | 14·0 |
| Bluish-green | 11·8 | 12·3 | 12·0 | 11·9 | 13·3 | 12·8 |
| Green | 13·5 | 14·7 | 14·1 | 16·3 | 17·2 | 17·6 |
| Flavazine | 8·5 | 8·5 | 8·5 | 12·9 | 15·1 | 13·9 |
| Flavazine with didymium | 11·5 | 11·6 | 11·0 | 16·6 | 17·0 | 18·0 |
| Red | 9·9 | 11·9 | 10·9 | 14·3 | 16·2 | 16·3 |

| | Sun, 33° up. Sept. 22. | Sun, 33° up. Sept. 28 | Sun, 33° up. Sept. 28. | Moon, Sept. 26, Moon 33° up. | | Basalt, fresh. | Basalt, weathered. |
|---|---|---|---|---|---|---|---|
| Ultra-violet glass | 14·9 | 15·8 | 14·9 | 14·9 | 15·0 | 14·9 | 16·2 |
| Cobalt glass | 14·3 | 15·2 | 14·6 | 15·2 | 15·0 | 14·4 | 15·6 |
| Bluish-green | 11·7 | 12·9 | 13·2 | 11·4 | 12·0 | 11·3 | 11·5 |
| Green | 13·2 | 14·1 | 15·5 | 14·0 | 14·2 | 13·1 | 12·3 |
| Flavazine | 7·0 | 8·0 | 8·8 | 7·5 | 7·4 | 7·8 | 5·5 |
| Flavazine with didymium | 10·7 | 11·0 | 12·2 | 11·3 | 10·7 | 10·6 | 8·8 |
| Red | 9·0 | 10·8 | 11·5 | 9·5 | 8·7 | 9·3 | 7·4 |

The next series of experiments were designed to include in the comparison the direct light of the sun and moon. These give approximately parallel rays, which traverse the absorbing screens normally. For comparison with them, it is desirable to restrict the cone of rays from the night (or day) sky as far as other conditions will allow. An aperture, 15in. in diameter, was placed 15in. from the plate. This aperture was the smallest that could well be used. The work was carried out in August and September and early October, when the hours of complete darkness are very limited. Summer time imposes a further obstacle The moon must be below the horizon, and the night should be clear. With the aperture ratio 1 : 1, as described, about nine hours' exposure were needed to give satisfactory intensity..

Two plates with this exposure were all I could get before my enforced return to London in October. The exposures were made at Beaufront Castle, three miles from Hexham, Northumberland, and also at Terling Place, Essex. There was no appreciable interference from town light, diffused by the sky.

In making exposures to direct sunlight, the difficulty was to reduce the photographic effect sufficiently. The ideal method would be to use a pinhole camera, giving an image of the sun which would cover the quarter plate used, but this involves an impractically long camera. To work at a reasonable distance, more divergence of the rays is essential. It was got by means of a quartz lens, of 7 mm. diameter and 9 mm. focus. The plate was placed on the axis of the lens, at about 60 cm. distance, when the divergent cone of rays from the image covered an area more than large enough The lens was mounted in the end of a blackened box, with a kodak photographic shutter over it. The plate holder, carrying the coloured screens and photometric wedge, was introduced at the other end of the box. A simple shadow arrangement was provided for pointing the axis of the lens at the sun.

A quartz lens was used, so as to avoid any absorption of ultra-violet light, or any risk of introducing colour which might disturb the comparison of sunlight with other sources.

Exposures were also made on direct moonlight. For these, no special arrangements were needed, as an exposure of several seconds proved suitable.

The results are given in Table II.

In considering these results, it will be noticed in the first place that the wedge readings for cobalt glass and bluish-green glass respectively are nearly the same whatever the source of light. This merely expresses the fact that by far the greater part of the photographic effect of the spectrum is due to the kind of light which these glasses can transmit. In any case, the ultra-violet or red ends of the spectrum produce a comparatively small fraction of the whole effect, consequently the absence or presence of these constituents hardly affects the wedge reading for the blue.

It is in the case of the ultra-violet at one end of the spectrum and the yellow and red at the other that enough variability is to be expected to give information as to the constitution of the source.

The ultra-violet constituent tends to be variable for plates obtained on different occasions. This is not surprising when we consider that this constituent is largely affected by atmospheric absorption, and is therefore sensitive to atmospheric conditions, even when the sky is apparently clear. For the same reason this constituent will be largely affected by the altitude of the source. Thus he sun and moon, both exposed to at 33° altitude, are at a disadvantage compared with the zenith sky.

For these reasons not much can be inferred from the ultra-violet data. It is noteworthy, however, that the zenith sky seems much richer in this constituent when the sun is high, than at sunset. This may be accounted for by atmospheric absorption of the rays from the low sun before they reach the observer's zenith, and are scattered towards him by the air.

The great superiority of the night sky over the day sky in yellow and red light is again apparent, amounting as before to about 4 scale divisions (a factor of 2·5).

The night sky also differs very little in quality from direct sunlight. It is only in the ultra-violet that any definite distinction is apparent, and as

already remarked, the zenith sky would have an advantage in this region on account of less atmospheric absorption.

No definite distinction can be made from these experiments between the chromatic constitution of sunlight and that of moonlight. The numbers found are same within the limits of experimental error.

We may say therefore that the night sky is found to be of the same colour as direct sunlight or moonlight, but much yellower than the clear day sky.

*Colour of Moonlight.*

What we can see of the moon's surface suggests that it consists of volcanic rock, and the light is, of course, diffusely reflected sunlight. It occurred to me, in connection with the present experiments, to include in the comparison sunlight diffused from specimens of terrestial volcanic rock. These exposures were made when the sun was 33° up, so that atmospheric absorption should be as nearly as possible the same as when the moonlight exposures were made. The photographic plate was placed in the box used for exposures to direct sunlight, but the quartz lens was removed. The iris diaphragm attached to the shutter was adjusted so as to subtend half a degree at the photographic plate—the same angular diameter as the moon—and it was backed with the specimen of rock in full sunlight placed near the aperture. The same exposure was given as was given to direct moonlight Only two exposures were made, one to a specimen of fresh basalt, and another to a weathered ochreous surface of the same. The light from the fresh basalt cannot be distinguished definitely in quality from moonlight or sunlight, but the light from the weathered basalt appears to be distinctly yellower than moonlight. The experiments are too few for a final conclusion, but they suggest that the surface of the moon is more like the fresh than the weathered specimen. This is in accordance with the absence of a lunar atmosphere. (These experiments on rock were hampered by the fact that the photometric apparatus was not at hand when the exposures were made. They are merely of a preliminary character).

*Visual Observations on the Night Sky.*

The conclusions reached, photographically, on the night sky are entirely confirmed by visual observation.

The photometric comparison of lights of different colours is, under ordinary circumstances, difficult and embarrassing, and little definite significance attaches to the results. But with lights below a certain intensity this difficulty disappears, since there is no longer the power of colour discrimination, and vision is monochromatic. A confident decision can then be given as to which of two lights appears brighter, whether they are of the same spectral quality or not This is, of course, well known, and is fully elaborated in works on colour vision.

Two gelatine films on glass were prepared, one dyed yellow with flavazine, and the other with methylene blue, the intensity of the latter being adjusted by washing out some of the colour until right for getting the effects which will now be described. The two films were mounted edge to edge at the end of a pasteboard tube, so that, when the tube was directed to the sky, the circular field was seen divided into two along a diameter.

During the daytime the yellow film was considered by all observers to be the brighter. As twilight advanced, the Purkinje phenomenon came into evidence, and the blue film became brighter. This remained the case when the light had waned so far that the colour sensation had disappeared. As the stars came out, the predominance became less marked, and, before the Milky Way was distinguished, there was equality Finally, when the Milky Way was conspicuous, the yellow film was notably brighter, whether the tube was pointed to the Milky Way or to other parts of the sky.

Another pair of films was prepared, giving equal intensities when the night sky was viewed In this case, still more than in the previous one, the blue half appeared brighter while any twilight remained. (A preliminary notice of this result was published in a letter to *Nature*, dated August 20, 1920).

It was desired to confirm visually the conclusion reached by photography that the colour of the night sky was nearly the same as that of direct sunlight or moonlight. Moonlight was chosen, as being of more convenient intensity. It was found that the yellow and blue films, which appeared equally bright against the night sky, also appeared equally bright when viewed against a white cloth exposed to direct moonlight. This background was, however, somewhat too bright, and, in order to get rid of colour perception, it was found advisable to reduce it twelve-fold by means of Fox Talbot's revolving sector. It was then impossible to distinguish between the two coloured films, which appeared of exactly equal intensity.

The night sky was examined on many occasions through the pair of films, which gave equal brightness. I never observed any marked deviation from equality, at considerable altitudes, though low down the yellow often had an advantage. This is probably attributable to selective atmospheric absorption. The experiments gave no evidence of a variable colour such as might be produced by an aurora of variable intensity.

I may add that my own attempts to see or photograph the aurora line on ordinary nights have had no success. All that I could see was a continuous spectrum. *Note added, March* 4.—I have since succeeded in regularly photographing the aurora line.

*Summary and Conclusion.*

To get the information as to the chromatic character of the light from the sky at night, photographic exposures were made under coloured media selected for isolating various parts of the spectrum. By comparing the photographic densities obtained, it was concluded that the night sky was much yellower or less blue than the (clear) day sky. Comparison with direct sunlight or moonlight showed that the night sky was of the same quality as these.

Visual comparisons through coloured films showed that a blue film, which was equally bright with a yellow one against the night sky, was brighter against the twilight sky. These comparisons were not embarrassed by colour differences, because the light was so faint as to give purely monochromatic vision. The two films matched one another equally well, whether they were seen

against the Milky Way or against other parts of the sky. In the photographic work no special attention was paid to this point, the exposures being made to a considerable area of sky around the zenith. The diurnal motion, of course, brought successive areas of the sky into action during the long exposures.

One theory of the light of the night sky attributes it to sunlight scattered by a very rare gaseous atmosphere, situated so high up as to be outside the earth's shadow. The present observations are contradictory of this theory, which would require the night sky to have the same colour as the day sky.

The comparative absence of polarisation (see Rayleigh, *Astr. Jour.*, 1919, l., 227; also Babcock, *ibid.*, p. 228) leads to the same conclusion

The requirements, as regards colour and polarisation of the light, would be satisfied if we regarded it as coming from an unresolved background of stars. They would equally be satisfied if we regarded it as due to sunlight scattered by meteoric matter. The conclusions of van Rhyn (*Astro. Phys. Jour.*, 1919, l., 356) favour the latter alternative. He regards the general light of the sky as an extension of the zodiacal light.

## THE PRESENT POSITION OF SMOKELESS FUELS.*

By F. S. SINNATT, M.B.E., M.Sc. (Tech.), F.I.C, M.I.Min.E., Lecturer in Fuels, College of Technology, Director of Research, Lancashire and Cheshire Coal Research Association.

THE commercial literature on the subject of smokeless fuels is considerable, and it appears desirable to collect together the material in order to attempt to ascertain the general lines along which the industry concerned with the manufacture of artificial fuels by carbonisation of coal is proceeding.

It is not proposed to discuss the relative advantages of gas, electricty, and smokeless fuels, but to assume that there are many people who wish to have a fire of solid fuel in certain rooms in their houses; this desire may be largely sentimental, but many hold that solid fires are more healthy. Everyone wishes to reduce the black smoke and and fog-nuisance, especially in large towns, and the householder is offered four main alternatives, gas fires, electric heating, central heating, or smokeless fuel fires.

It is generally recognised that coke, as obtained from gas-works, is not entirely suitable for combustion in ordinary grates, owing to the difficulty with which it ignites, but if a sufficient supply of good coke were available, the need for smokeless fuels would not be so pronounced. In modern gasworks there is a tendency to produce increasingly large volumes of gas, and if it is assumed that the coal-tar and ammonia are still important by-products, the increased volume can only be produced at the expense of the coke, with the result that the percentage of inorganic constituents in it becomes excessively high, and cases can be cited of coke containing as high as 20 to 30 per cent of ash and a considerable percentage of water. Such fuel as this is not suitable for domestic fires, and to offer such material for household purposes is an injustice to the small consumer who is at the mercy of the gasworks, and an injury to the movement for the wider use of this fuel. This tendency in modern gasworks reaches its culminating point in the comparatively modern process of converting the whole of the coal into gas, without producing any coke. The consequence of the above is that many households which formerly used coke have now to burn coal if they wish to have a solid fuel. It therefore appears that, although the larger production of gas is a step forward, and leads to a decrease in the smoke nuisance, there is, on the reverse side, a greater use of coal to replace the coke which was obtained from the gasworks. The shortage of suitable coke makes it desirable for the industry producing smokeless fuels to be developed in order that a supply should be available.

Many of the processes for the manufacture of smokeless fuel are in an experimental state, but certain of them have made sufficient progress to indicate that they may become large industrial processes.

*Requirements of Smokeless Fuel.*—The manufacture of smokeless fuel is, in itself, a sufficient incentive for the carbonisation of coal at a low temperature, but the principle involved has certain additional advantages which must receive notice. Thus, the weight of the products per ton compared with those obtained in ordinary gasworks, is as shown in Table I

The amount of tar obtained is much greater than that obtained at a high temperature, whilst the amount of ammonia and the volume of gas are considerably less. The efficient separation and utilisation of the tars from the low temperature carbonisation of coal have not been completely solved, and considerable research work is still required. The products from the tar are compounds, belonging to the aliphatic or associated series, as distinct from those present in the tar from the high temperature carbonisation, which contains compounds of the benzene series. Both these series of compounds have special commercial applications, but whereas the benzene (high temperature carbonisation) is of vast importance to the following industries—coal tar colour, disinfectant, motor fuel, and explosives—the compounds obtained from the low temperature carbonisation are chiefly of importance in two industries only, for motor fuels and for lubricants. It is obvious that the products are not so valuable as those obtained from ordinary coal-tar.

The volume of gas produced is considerably smaller than in high temperature carbonisation, but it would appear that this gas may find other application than burning for ordinary purposes.

The reasons for the necessity for smokeless fuels are economy in the burning of coal, shortage of coke (and that available is of inferior quality), reduction of the number of fogs, economy due to clean buildings, reduction of the amount of washing and cleaning in the household.

Smokeless fuel should possess some of the following characteristics: It must be smokeless and ignite with ease; it should not be too fragile so that it can be handled with safety, and should not be too bulky; should not absorb water, and, if it becomes wet, it should dry in a reasonable time. It should have a low ash-content, which should

* Excerpt from the *Journal of The Royal Sanitary Institute*, 1921, xlii, No. 1.

TABLE I.

| | High Temperature Gas Works. | High Temperature Coke Oven. | Low Temperature. |
|---|---|---|---|
| Gas ... ... ... .. ... ... | 12,000 cu. ft. (550 B.Th.Us.) | 11,500 cu. ft. (450 B.Th.Us.) | 6,000 cu. ft. (750 B.Th.Us.) |
| Tar ... ... ... ... ... ... | 10 gallons | 8 gallons | 20 gallons |
| Coke ... ... ... ... ... | 13½cwt. | 14·4cwt. | 14·5cwt. |
| Ammonium Sulphate ... ... | 25lb. | 28lb. | 15lb. |

TABLE II.—*Smokeless Fuels: Chemical Analyses.*

| Percentage. | Lignite Low Temperature. | Carbo-coal | Briquette Sun Fuel Co. | Hargreaves Coke. | Special Briquette. | Low temp. Carbon Coke. |
|---|---|---|---|---|---|---|
| Water ... ... ... ... ... ... ... | 6·44 | 2·03 | 3·10 | 0·60 | 2·60 | 2·42 |
| Ash ... ... ... ... ... ... ... ... | 16·85 | 15·66 | 10·48 | 10·70 | 9·00 | 4·70 |
| Volatile matter ... ... ... ... ... | 22·43 | 5·94 | 10·08 | 7·80 | 13·00 | 15·45 |
| Volatile organic matter ... ... ... | 15·99 | 3·91 | 6·98 | 7·20 | 10·40 | 13·03 |
| Coke ...... ... ... ... ... ... ... | 77·57 | 94·06 | 89·92 | 92·20 | 87·00 | 84·55 |
| Fixed carbon ... ... ... ... ... ... | 60·72 | 78·40 | 79·44 | 81·5 | 78·00 | 79·85 |
| Calorific value B.Th.U. per lb. ... | 10,280 | 11,570 | 12,740 | 13,180 | 12,400 | 13,550 |

not be powdery; must contain only a small percentage of sulphur; must be of a porous nature so that its combustion will not take place only from the outside, but enter into the texture of the material, in order that the ash which is formed does not cover the surface of the fuel and prevent combustion.

The following is a list of smokeless fuels with which the author is acquainted: Low Temperature Carbonisation Fuel, Tarless Fuel, Carbocoal, Coke Briquettes, Lignite Utilisation Board Fuel and Exors, J. Hargreaves Coke. Others have been mentioned in the literature, but no specimens have been examined by the author.

*Low Temperature Carbonisation Fuel.*—The coal used is washed bituminous slack, and is conveyed into hoppers which contain the exact charge required for a retort. The charge remains in the hopper until the previous charge in the retort is carbonised, and during this period it absorbs an appreciable amount of heat from the tops of the retort. Between the hopper and the retort is a rotary door, which, when open, allows the coal to fall gently into it. At the bottom of the retort is a similar rotary door for discharging the product. Below this door is a gas-tight chamber, into which the material is admitted when the carbonisation is complete, and it remains here until the succeeding charge is ready to leave the retort. When the coke door is opened, the original charge, which has now become quite cool, passes from the chamber. The low temperature coke is kept within the air-tight chamber in order to prevent loss of volatile constituents and deterioration due to burning in the air, and it was found objectionable to cool it by means of steam, as this changed the colour from black to grey. The retorts are built of refractory material, but experiments are in progress on the use of cast-iron, in order to ascertain whether this can be applied The figures given in Table I. are quoted from a paper by Mr. Davidson, given before the Institution of Engineers, Bradford, December 13, 1920.

*Tarless Fuel.*—This process indicates a novel treatment. The coal was carbonised in specially designed (Tozer patent) vertical retorts of cast iron, arranged so that the coal was carbonised in layers not thicker than about 5in. The carbonisation was carried out at about 550-600° C. under a pressure of about 3in. of mercury (vacuum 25in. of mercury). The products of carbonisation were drawn from the coal, leaving a residue which was a perfect smokeless fuel.

*Carbocoal.*—The manufacture of carbocoal introduces a new principle: The pulverised coal is fed into horizontal retorts, 20ft. long, 7ft. in diameter, lined with carborundum, and fitted with two overlapping series of arms attached to two revolving shafts. The coal is stirred throughout the low temperature carbonisation, and is gradually forced to the outlet of the retort, where it is automatically discharged. This process is a continuous one, and is conducted at a temperature of about 500° C. The coke obtained by the above treatment is in a state of very fine powder, and from the ordinary point of view is valueless. It is, therefore, mixed with pitch as a binding material obtained from the oils distilled in the plant, and made into briquettes, generally egg-shaped; the briquettes are fed into an inclined retort, heated to a temperature of 1000° C. The coke and pitch now undergo a second carbonisation at the temperature generally prevailing in ordinary coal gasworks. The result is that the coal is deprived of practically all its volatile products, and the pitch is also decomposed, whilst the fuel which leaves the plant is a coke-briquette. The fuel has certain distinct features: it is compact, tenacious, non-fragile, but, from experiments carried out by the author, somewhat difficult to ignite.

*Lignite Utilisation Board Briquettes.*—This process has been designed specially to deal with the lignite which has been found in large quantities in Canada. It consists in carbonising the material in a finely pulverised state, in a retort so inclined that the material is fairly free in moving through it. The lignite is non-caking. The carbonisation is carried out at a low temeperature, and the resulting coke is mixed with a binding material and briquetted at a temperature of about 300° C. The resulting fuel is a perfect type of briquette, which is practically smokeless. This process is of some interest in view of the large amount of lignite which is available throughout the British Empire, and which has not received the attention it merits, largely owing to the fact that its calorific value appears too low to be an economical

product to work. It would appear that by carbonising and subsequent briquetting, it is possible to convert it into a fuel having a distinctly high calorific value (see analyses).

*Carbon Smokeless Fuel Briquettes* (*Sun Fuel Co.*).—One part of bituminous coal is mixed with three parts of anthracite coal (by weight), and water is added to the finely powdered mixture up to about 12 to 15 per cent. The stiff paste thus formed is pressed into two sets of moulds, which, when placed face to face, are automatically locked together, and passed through a carbonising chamber at 700 to 900° C. for 15 minutes.

The volatile matter evolved amounts to about 14 to 17 per cent, and the resulting briquette is a coked mass, in which the carbonisation of the bituminous coal has led to the agglutination and binding of the anthracite.

The proportions of bituminous and anthracite coal may be varied according to the quality of the former.

*Exors. J. Hargreaves Low Temperature Coke.*—Experiments have been carried out upon the low temperature carbonisation of coal in a modified coke-oven, with a view to determining whether a suitable product could be obtained. These have proved successful, and a compact fuel has been produced containing up to 12 per cent of volatile matter, and burning freely. The coal used was Mountain Mine coal, which has a very high caking power. The product is a very excellent smokeless fuel.

*Testing Smokeless Fuels.*—No convenient method of determining the relative values of different smokeless fuels has been developed Trials on a standard grate are laborious and impossible for the ordinary consumer. It was, therefore, considerd to be of interest to place on record the values for two requirements, which are of some importance, the proportion of volatile matter present and the texture or micro-structure of the coke. These two features are important, as they indicate the approximate properties and the ease with which the fuel will ignite and continue to burn. Fuels low in volatile matter will be difficult to ignite, and burn sluggishly. If the texture is very porous, the material will be fragile and burn rapidly, whilst if too compact the reverse will be the case.

Table II. shows the approximate analyses of specimens which the author has received. It should be recognised that the percentage of ash depends largely on the kind of coal used.

*Conclusion.*—From the above it will be gathered that the industry is, at present, in its infancy, relatively to the coal-gas, coke,, or coal industry, and that in this country, with the exception of the Low Temperature Carbonisation process, it may be said to be in an experimental state. It appears desirable that collieries or gasworks, or both, should undertake the manufacture of some type of smokeless fuel. Such an undertaking would solve the problems of fuel-conservation, air-pollution, and efficient heating for our houses. Under such an ideal state of affairs the coal could be worked at the pithead, or in conjunction with coal-gas.

I have to thank Mr. A. McCulloch, A.I.C., for help in the preparation of this paper. The work was carried out under the auspices of the Lancashire and Cheshire Coal Research Association.

# THE RAJPUTANA SALT INDUSTRY.

By P. C. SCOTT O'CONNOR,
Deputy Commissioner, Northern India Salt Revenue

THE whole of the tract of country knowns as Rajputana is, generally speaking, saline in character. Most of the deeper wells are brackish, and in the summer months the water in certain areas is undrinkable. The people depend largely on rain-water, which is conserved in tanks or stored in small reservoirs constructed underground. For a few months after the rains, however, fresh water in small quantities is to be had a few feet below the surface, and this is obtained from shallow holes dug in the sand.

All the natural depressions in the country are capable of producing salt. The most important of these is the salt lake at Sambhar which is the largest of its kind in India. It lies at an elevation of 1184ft. above sea-level. In shape it is somewhat oval, with a length, from east to west, of about twenty miles, and abreadth varying from two to seven miles. On the west it is bounded by the Aravali range of hills; on the other sides there are vast sand plains. In area it is about 90 square miles. The bed slopes very gradually to the centre, where the depth, when the basin is full, is about 4½ft. A little over 100 years ago, the water stretched for 50 miles, and there is no doubt but that the two depressions in the neighbourhood, known as the "Nallia Sur" and the "Julga," which are now separate lakes, were at one time merged in the great lake.

Local tradition ascribes the formation of the lake to the gift of the goddess Sakumbri Devi, the tutelary goddess of the Chauhan Rajputs, who, in return for milk supplied to a religious ascetic in A.D 551, converted the forest into a vast plain covered with gold and silver. As the inhabitants of the locality regarded the gift more in the light of a curse than a blessing, fearing it would excite the cupidity of the neighbouring clans, the goddess turned the precious metals into salt which the rain dissolved and washed into a natural hollow, thus forming a lake. It is a pretty story, and one that is still credited by the simple-minded Rajput folk. In 1870, when we finally took over the administration of the lake, a peculiar incident occurred which greatly excited the people, as they thought we had discovered the means of winning back the original gift of the goddess. The Government chemical analyst, in search for a little pure silver, converted some metallic silver into chloride of silver, and mixing this with some borax to act as a flux, placed the whole white mass in a crucible and made it over to a village goldsmith to be reduced to its metallic form. When a sufficient degree of heat had been reached the workers were astonished to see molten silver in the crucible. The *rationale* of the process had to be explained to the local state officials and the leading men of the town before they would be convinced that there was no magic about it.

Science teaches us that the large majority of the salt lakes of the world have been formed, either by isolation of bodies of sea-water or by the solution of rock-salt, or by the combination of the two. Good examples of these processes are the Dead Sea, and the Bitter Lake in the Suez Canal; but there are other lakes, such as Lake Oroomiah in Persia, which are formed by rainwater and

streams dissolving effloresced salt and carrying the brine into natural basins, which, having no outlet, concentrate by evaporation. In regard to the Sambhar lake, it was thought at one time that the formation of the depression and the salinity of the water were caused by subterranean rock solution; but borings have failed to show any trace of rock salt underlying the bed of the lake, nor is there any evidence of such salt anywhere in Rajputana. The theory, therefore, that the salt in the lake is derived from the denudation of the rocks of the surrounding country which were once assumed to belong to the Permian system, a system abounding in limestone and salt, does not appear to be the correct explanation. It was also conjectured that, at some past period of the world's history, the sea receded from the present sandy wastes of Rajputana, leaving the soil impregnated with salt, which was gradually washed by rain into the natural depressions in the country. As millions of tons of salt have been taken out of the lake in the past, and spontaneous or naturally-formed salt is no longer obtainable, it was thought that the supply of salt was becoming exhausted; but investigations made by Sir Thomas Holland and Dr. Christie show that there has been no appreciable diminuution of the stock of salt, which is sufficient to meet all demands for a practically unlimited period; and, moreover, that the supply is being contributed to from year to year by dust salt brought in by the summer winds from the sea. The disappearance of spontaneous salt is due entirely to the inflow of silt, which has buried a large part of the bed of the lake.

In a paper on "The Origin of the Salt Deposits of Rajputana," published in the Records of the Geological Survey of India in 1909, Sir Thomas Holland wrote :—

"Investigations have shown that the salt resources of Sambhar are confined to a body of saliferous silt, stretching over an area of 80 to 90 square miles, and attaining depths in the centre of 60 to 70 feet. The analyses made of samples taken at regular intervals over the lake-bed show that in the upper four feet of silt, over an area of 63 square miles, there is an accumulation of more than 18,000,000 tons of salt." In regard to the salt blown in from the sea, it is stated that it is "brought in in the form of fine dust by the strong south-west winds that blow across the salt-encrusted region of the Runn of Cutch during the months of April, May, and June of each year," and that in the monsoon "the finely-divided salt dust that may have reached the heart of the desert is washed into the hollows occupied by brine lakes."

The upper two feet of the bed of the lake are composed of black, fœtid mud, giving off sulphuretted hydrogen, derived from the decomposition of animal and vegetable matter, which is the cause of the characteristic and unpleasant smell often noticeable.

The lake has no outlet, but there are four streams—the Menda, Rupnagar, Kharian, and Khandel—which flow into it. These streams, with their tributaries, drain an area of no less than 2200 square miles: consequently, in a year of heavy rainfall, such as 1917, when the fall measured over 41in., as against an average of 20in., the lake fills to overflowing. In the early summer months, when the lake is dry, the glare and heat are intolerable, and the whole country presents a picture of the greatest desolation; but during the rains a marvellous change takes place. The scenery then is exceptionally fine, and the sunset effects are the most gorgeous I have witnessed on the plains of India. Particularly interesting is a visit on a breezy moonlight night to the embankment which guards the salt works from the main body of the lake. The heaving mass of water, the sparkling, foam-crested waves, the boom of the surf, the smell of the air, all remind one of the sea, and, as one gazes westward, visions of white cliffs emerge from the background of the sky.

The lake lies within the boundaries of the States of Jaipur and Jodhpur. The western half is owned by Jodhpur, while the eastern half is owned jointly by the two States. The population in the neighbourhood is sparse, owing to the sterility of the country, but there are two towns, Sambhar and Nawa, wit ha population of about 12,000 and 5,000 respectively, situated on the shores of the lake itself. The lake was worked by the Emperor Akbar and his successors up to Ahmad Shah, when it reverted to the Rajput Chiefs of Jaipur and Jodhpur. From 1835 to 1844 it was worked by the Indian Government to repay them for compensation due and expenses incurred in repelling the predatory raids of the Rajput tribes in British India. On February 1, 1870, it was leased to the Indian Government, since when it has remained under our administration. The principal object which Government had in view in obtaining a lease of the lake was to increase the supply of salt and reduce its price in the United Provinces of Agra and Oudh by providing skilled supervision and improving communication between it and the markets. Prior to its acquisition by the Indian Government, the Salt Department of Northern India, then known as the Inland Customs Department, was not concerned with the manufacture of salt. The great Customs Line—a chain of posts, 2472 miles in length—stretched across India from Torbela on the Indus to the Mahanadi, in the Central Province, and duty was collected at the *chaukis* on the line on salt coming up from the Rajputana sources, destined for British India. By 1878 the Indian Government had assumed the management of the remaining sources in the Jodhpur State, and had negotiated treaties with all the other Rajputana Chiefs within whose territories salt was being manufactured, enjoining the closure of the works, on payment of compensation, or the restriction of the output at works left open under the management of the Darbars. Duty was now levied at the sources and the Customs Line abolished. The sums paid under these treaties to the Darbars, including the payments made for the Sambhar lake, amount to nearly 35 lakhs of rupees a year, and some of the principal States also receive a fixed quantity of salt yearly, either free of price and duty or on payment of half the duty only.

In the early years of our management, the Sambhar lake had not the importance which it now possesses as a source of supply. The average quantity of salt annually manufactured during the six years from 1870-71 to 1875-76 was 16,56,956 maunds, whereas the average quantity put up during the past six years was 55,63,265

The greatest quantity manufactured in any one year was 1,11,90,738 maunds in 1918-19. Since 1870, the lake has yielded over 20 crores of maunds of salt. Sambhar salt is in general use throughout Rajputana, and is extensively consumed in the United Provinces and Central India. Lesser quantities are exported to the Punjab and Bihar. During the war, when the supply of imported salts fell off, the demand for Sambhar salt from Bihar rose considerably and some was also sent, for the first time, to Bengal. Now that foreign imports have increased, the demand from Bengal has practically ceased, while the exports to Bihar have fallen to about one-fourth of the war-time demand; but the quantity is still about five times as much as in pre-war times.

In the dry, hot air of the desert, eveaporation is rapid, and within a few months after the rains, in a year of normal rainfall, the waters of the lake contract and gather towards its central and deeper parts, where, after further evaporation, a wide bed of spontaneous salt is exposed to view. Owing, however, to the belt of soft mud by which this salt is surrounded, it is impossible, except at a prohibitive cost, to gather it and bring it to store. Spontaneous salt is, therefore, no longer gathered, and all the salt now obtained from the lake is manufactured. Salt is won by two methods: from permanent salt works constructed in the bed of the lake and called *kyars*, and from shallow pans of a temporary nature constructed on the lake shore. The former are worked by the Department and the latter by contractors. A kyar is a large rectangular enclosure divided into pans and protected from the lake water by high embankments pitched with stone. Alongside the kyars are platforms for the storage of salt and reservoirs for brine. Before the monsoon sets in, the mother-liquor (otherwise known as "bitterns") which is the concentrated residual brine from which the salt has separated, is pumped out of the pans, which are then cleaned and prepared for the following season's crop. As soon as the rains have ceased, the sluice gates of the reservoirs, which have been left open during the monsoon for the admission of brine, are closed, and as much extra brine as the reservoirs will hold is pumped into them. If the rains have been heavy and the kyar pans are flooded, the excess brine is pumped out, while if they are not full enough, brine is added. In a normal year the brine in the pans, after the rain, has a density of about 10° Beaume, and it is the object of the manufacturing officer so to keep his pans supplied with brine as to have a depth of 12in. when the density has risen by evaporation to 25° B This will leave him about 4in. of brine when the density has reached 29° B. or 30° B., when extraction of salt begins. This depth of brine is essential to keep in solution the magnesium and other undesired salts which may be present and is also required for the washing of the gathered salt.

The lake brine is a complex solution of sodium chloride (sodium sulphate, sodium carbonate, calcium carbonate, and a trace of magnesium salts. Now the object of the salt manufacturer is to extract the sodium chloride as free from the other salts as circumstances will permit. To enable him to do this, it is necessary that he should not only be acquainted with the various salts in the brine, but should also study their behaviour and mutual reactions in solutions of various degress of concentration at different temperatures. An instrument, known as Beaume's hydrometer, designed to show the density of fluids, will tell him how the evaporation of his brine is progressing, and what changes are taking place in it; but, as the presence of other salts in the brine affect its reading, experience alone will enable him to correct the error in practice, and visual examination of the salt crust, from day to day, will help him to decide when to begin extraction and when to stop it. Further, it is imperative that he should observe closely all changes in the weather, as such changes materially affect the quantity and quality of the salt manufactured.

The extraction of salt at the lake is done entirely by manual labour. As soon as the salt has formed, labourers—men, women, and children—enter the pan and gather up the crust into small heaps. Some skill is required in this operation to avoid taking up the mud on which the crust lies. After the heaps have been thoroughly washed with residual brine and allowed to dry, the salt is carried in baskets, by headloads, and in bags on buffaloes, to the storage platform, where it is built up into conical and oblong pyramids, sloped to an angle of 36°—the angle of repose for granular, loose salt—and containing from 50,000 to 1,00,000 maunds each. These heaps are beaten and smoothed as a protection from rain, but not covered. The wastage amounts to about 3in. of surface salt per annum. Formerly payment was made on estimation at the close of the day's work to each labourer separately for the salt he had put up. This necessitated the making of innumerable little heaplets on the storage platform preparatory to the removal of the salt to the main heap. Now a very much better system has been introduced, and has resulted in a considerable saving of time and energy to all concerned. A contractor has been appointed, and the labourers are paid by him for each basket of salt as it passes his overseer on its way fro mthe pan to the main heap, the contractor himself being paid on the estimated contents of the main heaps, payment being made fortnightly.

If extraction is begun at the right time, and all dirt and insoluble matter washed or pciked out, Sambhar kyar salt is of excellent quality. The crystals are large, hard, and white. Representative samples have on analysis been found to contain over 99 per cent of sodium chloride.

Pan salt is made by private contractors in shallow pans on the shores of the lake. These works are of a temporary nature, constructed each year after the monsoon. Brine is obtained from wells dug in the bed of the lake. The produce is white, and of fair quality, but, as the crystals are small, due to the shallowness of the pans used, this variety is not much in favour with traders as it loses weight in transit.

Twenty years ago there were eleven kyars at the lake, covering an area of about 736 acres; but two more kyars have since been constructed and it is proposed to add another. As the labour formerly employed by pan contractors is now employed in the kyars, the manufacture of pan salt is fast dying out.

The cost of production is about 1 anna and 2 pies per maund of kyar salt, and 7½ pies per

maund of pan salt. These figures include the cost of upkeep of works and interest on capital sunk. The salt is sold at the source at a uniform price of 4 annas a maund, and the duty is Rs1-4-0 a maund.

As will already have been noticed, the manufacture of salt at the Sambhar lake is dependent to a large extent on the monsoon rainfall. Given favourable conditions, no more than two crops of salt can be obtained in a season with the existing plant; but, as even this quantity is barely sufficient to meet the demand, the difficulty experienced by the Department when the monsoon fails can easily be imagined. Some years ago, when spontaneous salt could no longer be obtained at a reasonable cost, the works were enlarged by the addition of two kyars, and canals were constructed in the bed of the lake for the supply of subsoil brine; but the latter have not proved a success as they silt up very rapidly and cost a great deal to keep in working order. Moreover, the salt produced from such brine is inferior in quality.

Before the war, little, if any, effort was made to develop the sources and push sales. Times, however, have changed, and what satisfied us yesterday does not satisfy us to-day. The services of technical experts have been secured, and the aim of the Department now is, not only to meet the present demand, but to win new markets for its produce. There is no reason whatever why India should not produce all the salt she requires. With so extensive a seaboard and such vast deposits of salt as are found inland, and an ideal climate for manufacture, she ought not to have need of large imports of foreign salts. Nature has equipped her admirably with the means, and she is in a position to supply the requirements of her teeming millions without outside help.

Schemes for the thorough development of the sources have been worked out by experts. Some of these have, in whole or in part, been sanctioned, while others have been postponed owing to financial stringency. At Sambhar, a large reservoir—a long-felt need—is under construction. The comfort and welfare of the workers are receiving attention; and labour settlement, with comfortable quarters and a good water supply, is nearing completion. A new kyar, a central store, an efficient pumping plant, an electric installation and mechanical transport—all parts of the main scheme—are yet to come. These works will cost a substantial sum; but the money spent on them will be repaid several times over in a very short time by the profits that will accrue.

Provided, then, that the money required is sanctioned, the Department will in a few years be in a position to turn out salt of the finest quality in greatly increased quantities.—*Journal of Indian Industries and Labour.*

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Photography of Coloured Objects.—The advance in photography during recent years has been so rapid, and the results so far-reaching, that one cannot but feel surprised to read in a recent address by Sir William J. Pope, that "at the present time a very rapid panchromatic plate is on the market which is much faster to red than to blue light." Such a plate has very great possibilities.

## FUEL PROBLEMS OF THE FUTURE.*

By Sir GEORGE T. BEILBY, F.R.S.

(Continued from p. 102).

Considering next the production in the Empire outside the United Kingdom, molasses is the raw material which can be converted into alcohol most cheaply. Molasses is a bye-product of sugar refining; and the quantities available for the manufacture of alcohol are therfore dependent on the refined sugar output. The estimated Empire production of refined sugar in the season 1919-20 is just over one million tons; and the whole of the resulting molasses would only produce about 17 to 18 million gallons of 95 per cent alcohol. Considerable quantities of molasses are used in this country for the manufacture of industrial spirits. The output of the home distilleries equipped for the production of molasses alcohol is limited, however, to (say) some 7 or 8 million gallons of 95 per cent alcohol; and in view of the present cost of materials and labour and of freight, it would hardly be a commercial proposition to erect additional distilleries here for the purpose. It would be better to convert the molasses into alcohol where it is produced, to use the alcohol where it is made to supplement or replace petrol, and to export the balance. With the present increasing output of cane sugar, there should be very considerable quantities of molasses available for the manufacture of power alcohol; and the possibility of utilising these molasses is being brought to the notice of the authorities of the countries conerned. Even in the most favourable circumstances, however, the quantities of power alcohol available from this source must be (as shown above), comparatively small, and will in the first instance mainly be used in the neighbourhod of its production in replacement of petrol.

Some of the legislative questions which arise in connection with the use of alcohol for power purposes have been dealt with in the Finance Bill for this session. A section of the Bill provides for the use of a new description of methylated spirits, to be called "power methylated spirits," for generating mechanical power, and for the payment of the same allowance in respect of such methylated spirits as applies to methylated spirits used for industrial purposes—namely, 3d. a proof gallon. It also gives power to the Board of Customs and Excise to make regulations as to the composition and quantity of the denaturant. A denaturant will shortly be authorised for power methylated spirits, which it is hoped will reduce to the minimum the cost of denaturing spirits to be used for this purpose. Clauses will also be inserted in the forthcoming Revenue Bill extending facilities for the importation and distribution of spirits in bulk, and enabling the Board of Customs and Excise to make regulations providing for the use of alcohol in generating mechanical power. While it is necessary, in view of the high duty on spirits in this country, to maintain some restrictions upon their use free of duty, one result of the Government action will be that the production and use of alcohol for power purposes will be much facilitated, and the expense con-

*Delivered in the theatre of the Institution of Civil Engineers, London. Inserted by favour of the *Gas Journal*, June 29, 1921.

nected with any necessary restrictions will largely disappear.

As regards the work of the past year, Sir Frederic Nathan reports that experiments carried out on the cultivation of Jerusalem artichokes have indicated that very good yields of alcohol per acre could be obtained from them. These experiments are being repeated this year; and if the previous year's results are confirmed, it may be desirable to consider the possibility of growing this tuber to supply a limited quantity of alcohol for special purposes, such as aviation. An examination of the artichoke stems has indicated that it may be possible to convert them by simple treatment to paper pulp. Should this prove to be the case, both products would be cheapened.

The investigation as to the possibilities of producing alcohol in the Empire overseas are still in progress. So far as they have gone, they indicate that in the sugar growing countries, molasses, from which alcohol might be obtained, is being wasted, but that the quantities are comparatively small, and in most cases would be insufficient to meet even local requirements for alcohol. Alcohol might be made from suitable crops grown specially for the purpose in those Dominions and Colonies where labour is available, and used to supplement or to take the place of supplies from the above sources. Some such course is specially desirable where petrol is dear and difficult to obtain—for instance, in the East African Protectorates and West African Colonies, which are, moreover, very dependent on motor transport for their development.

The use of cellulosic materials is not yet possible, because though research work is in hand to find a process that could be employed on a commercial scale in those regions where such materials exist in sufficient abundance, it has not so far led to any definite results. Where, however, materials capable of easy hydrolysis exist (as, for instance, in the case of waste rice-straw), the recent large-scale experiments in Burma, carried out under the auspices of the Burma Oil Company, appear to indicate that the joint production of alcohol and paper should be a commercial possibility (see Sir Charles Bedford, *Jour. Roy. Soc. Arts,* June, 1921).

Until alcohol can be made from waste materials which can be collected and treated at small cost, it does not seem likely that Empire-produced alcohol can be imported into this country on any considerable scale; it is improbable that it can be produced cheaply enough or in sufficient quantities from materials grown for the purpose in those overseas portions of the Empire which will no doubt before long produce it in this way for local consumption.

The Finance Bill of 1921 contains clauses giving the Commissioners of Customs and Excise powers to make regulations with respect to spirits manufactured otherwise than by distillation, and with respect to the manufacture, storage, removal, sale, use, and supply of power methylated spirits, and the importation, storage, removal and use of spirits to be used in their manufacture.

Another of the fuel problems of the future is the winning and utilisation of peat. The history of the association of the Fuel Research Board with this problem has been given in various publications of the Department of Scientific and Industrial Research. Among these, the report of the Irish Peat Inquiry Committee, of which our past President (Sir John Purser Griffith) was the Chairman, stands out most conspicuously. This subject would in itself supply material for many lectures; but on the present occasion it can only be briefly referred to in its relation to the subject of our consideration to-night.

Reference has already been made to the extensive peat developments which are in progress in Germany. These are based on the experience gained at the Wiesmoor Peat Station, which has been in operation since 1910. The peat is dredged, macerated, and spread on the surface of the bog to dry. By stacking under cover, the moisture of the peat blocks can be reduced to 25 per cent solely by air-drying. It has been stated that, prior to the war, one ton of air-dried peat containing 25 per cent of moisture could be produced for 4 marks. For steam-raising purposes two tons of this peat are equal to about one ton of coal. At the Wiesmoor Station, eight water-tube boilers are fired by peat. The new stations in Germany are being designed on a much larger scale; no effort being spared to render them as perfect as possible.

These schemes appear to ignore the fundamental difficulty which applies to the winning of peat in quantities sufficient to meet the day-by-day requirements of any large central station. When it is realised that the peat deposit in a bog 20ft. deep is only the equivalent of a 12 or 14in. seam of coal, it will be evident that even an output of 1000 tons a day of air-dried peat involves the laying-out and development of an enormous surface. At the Zehlonbruck plant, near Königsberg, it is proposed to use 920,000 tons per annum, or about 2500 tons per day.

Prof. Purcell informs me that to win mechanically 900,000 tons of air-dried peat in one season, at least 4,500 men, women, and children would be required; and the area over which the spreading and drying operations would extend could not be less than 9000 acres, or (say) 15 square miles. He suggests that in dealing with any production, over 60,000 to 80,000 tons per annum from any single district, the difficulty would increase as the square of the production.

The Irish Peat Inquiry Committee was fully informed as to the position of peat winning in Germany prior to the war, and also as to the earlier survey and investigation work of the Canadian Department of Mines. In April, 1918, a Peat Committee was set up by the Federal Government in co-operation with the Government of the Province of Ontario, to investigate the possibility of manufacturing peat fuel on a commercial scale. The Alfred Peat Bog, on which the work of the Committee is being carried out, is about 43 miles east of Ottawa, and about 70 miles from Montreal. Last summer, Prof. Pierce Purcell, the Peat Investigation Officer of the Fuel Research Board, visited the experimental station at this bog, and carefully studied the results which had been achieved under the direction of Mr. E. V. Moore, the engineer in charge. Prof. Purcell was able to watch the harvesting operation over a period of weeks, and obtained much useful information as to machines and methods. His discussions with Mr. Moore were most useful; and on his return to this country he presented to the

Fuel Research Board an Exhaustive report on his visit. During the present season Prof. Purcell hopes to visit the peat stations in Sweden, Germany, Denmark, Holland, and France. We shall thus be in intimate touch with all the more important developments which are in progress; and the Fuel Research Board hope, by continuing the publication of full reports, to serve as a useful centre of information on the subject.

With regard to the Board's own activities, these were necessarily seriously curtailed by the war and the post-war conditions in Ireland. Last season (1920), however, peat was cut, macerated, spread on the bog at Turraun, air-dried, and harvested.

At the beginning of the present year, 100 tons of this air-dried peat were sent to the Fuel Research Station, where some interesting experiments were carried out on its use for boiler firing and for carbonisation. The peat when it reached the Station, contained about 27 per cent of moisture. After having been kept under cover for some months, the moisture was reduced to about 17 per cent. This peat is in the form of hard blocks of various lengths, up to about 10in., with a cross section of something like 2 by 2in. Its density is rather under 1, or about twice that of the ordinary hand-cut sods made on the same bog. The blocks can be sawn and cut like hard wood; and they stand transport with very little breaking-up into smalls. In this respect they contrast very favourably with the ordinary hand-cut sods, which break down seriously in transport by rail or road.

The result of last year's experience at Turraun shows that:—

(1) Machine peat dries more quickly than "cut peat" under equal weather conditions.

(2) Peat spread during August, and even as late as September 3, will have dried sufficiently—say to 35 per cent moisture—to be used as a fuel.

(3) It was possible in the wet and unfavourable season experienced to dry three separate spreadings of peat on the same area.

(4) The peat cut and spread as early as February 5 was little damaged by the rain and frost in the early part of the year, and was harvested, although four months were required to complete the process.

(5) The peat-winning season at Turraun extended over seven months last year—namely, from February 5 to September 3.

(6) Machine peat can be "footed" when containing 75 per cent moisture or less, and may be "clamped" when containing 40 to 50 per cent moisture. Slow final drying is necessary to get the best results with machine peat; and it is advisable that this should be done in a large "clamp"—the toughest blocks being thus produced.

(7) The season referred to had been one of the wettest experienced for some years. In six out of eight months, the rainfall exceeded the average for the past five years; and although June was a dry month, there were 163 rainy days in the eight months.

Steam-raising trials at the Fuel Research Station have shown that the peat in this form is an excellent fuel. Though the evaporative efficiency actually obtained was only 65·4 per cent, this was obviously due to the unsuitability of the furnace arrangements. Further trials will be made under more favourable conditions.

Peat blocks lend themselves admirably to carbonisation, either in vertical retorts at temperatures between 700° and 900° C., or in steel retorts at 550° to 600° C. The charcoal resulting from carbonisation is an ideal fuel for suction-gas producers. The oils obtained by carbonisation are now being examined.

As coal is likely to remain the chief source of fuel, not only for Great Britain, but for the world at large, the problems of its winning, preparation, and use, still occupy the foreground in all serious consideration of the subject. In the solution of these problems there is ample scope for the skill and enterprise of an increasing number of fuel experts and engineers, not only in the pioneering work of experiment and inquiry, but in the organisation and development of new methods as these are evolved.

In seeking to come to closer quarters with these questions, it may be helpful if we can set them out with some sense of proportion and perspective as they appear from the British point of view. We know, broadly, that in normal times before the war, the annual output of coal of the mines of the United Kingdom was approximately 287 million tons, of which 189 million tons were consumed as follows:—

| | | Million tons |
|---|---|---|
| 1 | Railways | 15·0 |
| 2. | Coasting steamers | 2·5 |
| 3. | Factories | 16·0 |
| 4. | Mines | 20·5 |
| 5. | Iron and Steel | 31·0 |
| 6. | Other metals | 1·3 |
| 7. | Brickworks, potteries, glass, and chemicals | 5·8 |
| 8. | Gas works | 18·0 |
| 9 | Domestic | 35·0 |
| | | 189·1 |

If from this total we deduct items 5, 6, and 8 (iron and steel, other metals, and gas works)—together say 50 million tons—the balance of 139 million tons represents the amount which is burned in the raw or natural state of the coal. The greatest of the fuel problems of the future is to decide what proportion of this huge total it will pay to subject to a preliminary operation of carbonisation of gasification, with the object of sorting out the potential thermal units of the coal into groups of higher availability or greater convenience as fuels—*e.g.*, gas, motor spirit, fuel oils, and coke.

Though the operations of carbonisation and gasification necessarily involve the expenditure and loss of some of the thermal units of the coal, so that the collective thermal value of the new fuels is less than that of the original coal, yet the loss may be more than compensated for by the increased value of some of the new fuels.

At the prices of to-day, a "therm" in the form of coal costs from 1d. to 2d., while in the form of motor spirit its cost is from 20d. to 25d., and in the form of town gas 10d. to 15d. These figures show the premiums which can be paid for the higher "availability" of special fuels. The general recognition of the value of availability and convenience of the more costly forms of fuel must not tempt us to overlook the necessity for a criti-

cal examination of the uses to which the more expensive fuels are being devoted.

In the case of motor spirit, there is a decided tendency to regard mere convenience as a sufficient justification for its use. While for swift transport by air and by road there is no cheaper substitute in sight, there are good grounds for believing that, for the heavier forms of motor traffic, motor spirit may be replaced by much less expensive fuels. A certain amount of success has already been attained in the use of small suction-gas producers in the slower and heavier classes of motor vehicles. The best hopeful prospect in this direction appears to me to be based on the designing of small suction-gas producers for definite types of solid fuel. The inventor too often feels that the success of his invention will depend on its adaptability to a great variety of conditons; and he fails to make any one successful design by attempting to deal simultaneously with a number of variables.

Small suction-gas producers for motor vehicles ought, in the first instance, to be definitely designed for, and worked with one definite type of solid fuel. Anthracite, low-temperature coke, wood, charcoal, and peat charcoal, each have their special characteristics, which will affect the design and working of the gas producer. The more important features which must be taken into account are: Freedom from tarry or oily impurities, density, inflammability, and the quantity and nature of the mineral ash.

Before considering in more detail the role of carbonisation and gasification at various temperatures as a means of sorting out from raw coal solid, liquid, and gaseous forms of fuel, let us pass in review very broadly the uses to which the 139 million tons of coal are put which are consumed in the raw state.

We all take our share in the consumption of the 35 million tons of coal which are devoted to domestic use; and most of us have a kindly feeling for our old friend the open fire. The work of Dr. Margaret Fishenden on open fires has definitely shown that, under reasonable conditions of firing, 20 per cent of the total potential heat of the raw coal is radiated into the room, and that a further 20 to 30 per cent is given up to the fabric of the building before the waste products of combustion leave the chimney. Smoke and soot are, however, an unduly heavy price to pay for the transient cheerfulness of the flaming coals in a well-stoked fire, especially when we remember that over long periods the ordinary fire is only smouldering and dreary looking. The coal-fired kitchen range, unlike the open room fire, has few, if any, sentimental associations, and its replacement by gas-cookers and coke-fired water heaters is only a matter of time.

I have for many years taken a deep interest in the production of a solid smokeless fuel for domestic purposes by the carbonisation of selected coals at 550° to 600° C. The resulting coke is entirely free from smoke-producing hydrocarbons, while still containing 10 to 12 per cent of volatile combustible matter, which burns with a slightly luminous, perfectly smokeless flame. When the coke is kindled, it becomes enveloped by these flames, which quickly raise the surface to incandescence. Undoubtedly, if this smokeless solid fuel could be introduced at a cost permitting of its being sold at little more than the price of the coal which it would replace, it would lead to a complete revolution in domestic heating, and, among other good things, to the abolition of black smoke from house fires. This attractive prospect has been spread before our eyes for many years by enthusiastic inventors and company promoters, yet its realisation seems always to move a little further into the future.

The problem really has two distinct sides—the technical and the economic. On the economic side, the data for a final solution will only be obtained after the technical solution has been reached. In other words, until a fair-sized industrial plant has been carried on continuously over a long period, making and disposing of all the products of carbonisation under steady market conditions, no one can say whether or not the business will be a profitable one.

On the engineering side, an efficient and not too costly apparatus must be designed and constructed in the working of which manual labour, fuel consumption, and maintenance costs are all reduced to a minimum. In these respects—as well as in its output capacity on a given ground area—the apparatus must stand comparison with gas-retorts and oil-shale retorts of the most modern types Only when this ideal has been practically realised can the future of low-temperature carbonisation as a business proposition be put to the test of continuous working on a large scale under the labour and market conditions of the day.

From the experience of the past two years at the Fuel Research Station with a considerable variety of coals, we know with certainty the yields and quality of the gas, oils, and coke produced under definite conditions; but this knowledge is only the first step in the inquiry. For, until we know with equal certainty the cost of producing these, and the markets in which they are to be disposed of, no economic balance-sheet of any real value can be arrived at.

Let me illustrate the market uncertainty by a few comparative figures. Assume that 15 gallons of fuel oil suitable for naval use can be obtained from a ton of coal. Six months ago the value of this oil could be safely taken at 1s. per gallon; and the 15 gallons would have realised 15s. To-day, the price of this oil is only 4d. per gallon; and the product would therefore only realise 5s.—a drop of 10s. per ton on the coal carbonised. It is obvious that a method of carbonising which would have paid its way handsomely six months ago would to-day result in a loss. My own belief is that low-temperature carbonisation can only be established on a sound commercial basis with low operating costs and a very moderate margin of profit

Prior to 1914, the shale-oil industry in Scotland was distilling three million tons of shale per annum. The entire cost of the carbonising operation, for labour, maintenance, and fuel was 1s. 6d. per ton; and the margin of profit on which fair dividends were paid was 2s. 6d. per ton. Unless the costs and profit margins of low-temperature carbonisation can be reduced to the modern equivalents of these figures, the prospects of its development on a great scale are not hopeful, from the national point of view.

If low-temperature carbonisation is proved to be a feasible operation commercially, it would

find it first and most natural application to the 35 million tons of coal used for domestic purposes. Were this coal all carbonised, it would produce about two million tons of fuel oil for the Navy, or considerably more than the peace requirements, though very much less than the war requirements. The motor spirit produced would amount to about 100 million gallons.

The capital expenditure required for the installation of carbonising plant for 35 million tons of coal per annum would be of the order of 30 to 40 millions sterling. A gross profit of 5s. per ton of coal carbonised would provide 10 per cent for interest, and 10 per cent for depreciation on this expenditure.

The application of low-temperature carbonisation to raw coal which is used in the industries must necessarily depend on the successful solution of the technical and engineering problems to which reference has been made. In this case also, the future possibilities of this application depend entirely in the evolution of apparatus and methods which will reduce the capital and working charges of the operation to a minimum.

(To be continued)

## NOTICES OF BOOKS.

*An Introduction to the Chemistry of Plant Products.* Vol. I. By Paul Haas, D.Sc., Ph.D., and T. G. Hill, A.R.C.S., F L.S. Third Edition. Pp. xiii.+414. 1921. London: Longmans, Green & Co. Price 16s. net.

With this edition, the authors have divided their treatise into two volumes: Volume I., which is essentially the same in scope as the earlier editions, deals primarily with the chemical side of the subject; but a sufficiency of plant physiology has been retained to make the book complete in itself. Vol. II., which is in preparation, will be devoted more to purely physiological problems. The present volume has been brought up-to-date, some portions have been re-written, for example, Section viii., which deals with the colloids, has been enlarged upon. The book consists of ten sections, each section dealing with a group of plants belonging to the same chemical family; for instance, Section i. deals with fats, oils, and waxes; Section ii with aldehydes; Section iii. with carbohydrates, &c. At the end of each section is given a short bibliography, to which the reader may turn for more detailed accounts of the subject under discussion.

*Ammonia and the Nitrides.* By E. B. Maxted. Pp. viii.+116. 1921. London: J. & A. Churchill & Co. Price. 7s. 6d.

In this small volume, the author briefly describes the researches of Haber, Le Rossignol, and others, on the synthesis of ammonia and the conditions which govern the equilibrium point, together with his own work on the synthesis of ammonia at very high temperatures. The results are carefully tabulated, and a clearly-written account of the experiments made, with good diagrams of the apparatus used, combine to make this section valuable alike to research workers and to students.

The second portion of the book, dealing with that little-known class of compounds—the nitrides—contains first an account of the general methods of preparation and properties of these bodies, followed by a short description of each one which has so far been obtained. The book concludes with a chapter on the work of Strutt, and the more recent work of Tiede and Domcke on the preparation, properties, and probable constitution of active nitrogen. All the information given is of the latest and most up-to-date character, and the book is both interesting and valuable to read.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences.* Vol. clxxiii., No. 5.

"The System Bromine-Tellurium. Nature of Tellurium Sub-bromide."—By M. A. Damiens.

"Preparation of Acyclic δ-diketones."—By M. E. E. Blaise.

## NOTES.

Board of Trade Announcement.—The attention of British subjects resident in this country who have pre-war debts owing to them from branches outside Germany of German undertakings whose head office is in Germany, is drawn to the fact that apart from their remedy against the branch, they may be entitled to claim payment alternatively from the head office through the Enemy Debts Clearing Office. In the event of there being any doubt as to the recovery of such debts from the branch, British creditors will be well advised to file a claim aganst th ehead office with the Enemy Debts Clearing Office, Cornwall House, London, S.E.1. It is essential, however, that any such claims should be received by the Clearing Office before September 30.

The *Manchester Guardian Commercial* says that as a sequel to the recent visit to this country of a delegation of American and Canadian dry goods merchants, it is proposed to set up a commercial entente between this country and America and the British Dominions. "I understand," says the London correspondent of this journal, "that it will be the business of the joint committee to set up a sort of clearing house of information between traders in the various countries who come into the scheme, whereby the interests of them all will be looked after in the various territories. Another feature of the scheme will be the arrangement of exchange visits to and from America and the Dominions of the sons and proteges of commercial men for the purpose of gaining for them wider business experience. Ultimately it is proposed to enlarge the scope of the undertaking by including other foreign textile organisations."

Tungsten Crystal Wire as Glow Lamp Filament.—O. Ely, in *Ver. deutsch. Ing. Zeitschr.*, 1918, lxii., 15-20. Abstract by Th. Verheggen in *Chem. Abstracts*, Feb. 20, 1919, xiii., 286-287.—After a brief historical review of the first metallic filament used in electric incandescent lamps, the different methods of manufacturing filaments for tungsten lamps are stated. The author then describes at length a new patented process (Julius Pintsch & Co., Berlin) for the manufacture of fila

ments made of a long crystal of metallic tungsten. "Manufacture of tungsten crystal wire: The $WO_3$ is pulverised as finely as possible, and is completely reduced by heating in a hydrogen atmosphere to produce pure tungsten metal, a brilliant black-brownish metallic powder. To this tungsten is added a carefully determined quantity of $ThO_2$ (and) finally a colloidal binding material is added in very small quantities. From this doughy mass filaments of various diameters are formed. . . . After the extruded "threads" have been dried at a moderate temperature, they are placed, eight at a time, into the treating apparatus, where the transformation into pure metallic crystals takes place. The treating apparatus consists essentially of a glass cylinder closed at both ends and provided with two contacts joined by a helix of heavy tungsten wire. The filaments to be treated are poassed through the axis of this glowing helix by means of a simple mechanism; during the operation . . . the filaments to be treated are raised rapidly to a temperature of 2600°-2700°. A continuous current of reducing gas passes through the glass cylinder. . . . The speed of movement through the hot zone must be less than the speed of crystallisation in order to allow the crystals to grow gradually at the expense of the small adjacent crystals. If the linear velocity of the filaments passing through the helix is too great a very fragile filament composed of several crystals is obtained . . . that breaks at the interfaces of the successive crystals. Filaments composed of a single tungsten crystal, unlike some drawn filaments, retain all their ductility and softness and resist vibration and shock even after many hours of burning; which is not the case with some drawn filaments. Comparative tests made under the same conditions with a lamp provided with a Pintsch tungsten crystal filament and lamp provided with a drawn tungsten filament have shown that after a life of 1200 hours, the filament made of a tungsten crystal had not given rise to the slightest trace of deposit on the walls of the bulb, whereas the filament of drawn wire was more or less disintegrated." Numerous photomicrographs of the new filaments and some of the old-fashioned filaments are shown.

HOP-GROWING EXPERIMENTS IN SOUTH AFRICA.—During 1920, 4,077cwt. of hops, valued at £68,047, were imported into the Union of South Africa for beer-making, and the average quantity imported annually during the previous five years was well over 4,000cwt., principally from the United Kingdom, the United States, and Australia. With a view to supplying the Union's requirements of this article, hop sets have been imported from time to time for purpose of experiment, and as far as experience goes, states the *Journal* of the Department of Agriculture of the Union of South Africa, it is found that the District of George, with its climate and conditions similar to those found in parts of Europe where hop-growing prevails, gives promise of being the most suitable part of the Union for this purpose; indeed, it is recorded that nearly a hundred years ago a successful experiment with hops was carried out in the town of George. The present experiments at George were started in 1918, and are now under the supervision of the botanist at the Elsenburg School of Agriculture. The object in view is to demonstrate that a sufficient return of green hops per acre can be obtained to make the cultivation of the crop an economic success. A good yield of dried hops is estimated at anything from 10cwt. per acre upwards; at George the drying process accounts for 65 to 75 per cent of the weight of the green crop, the average showing that about 100lb. of green hops yield 30lb. dry weight. Thus far, some of the sections in the experiments at George have shown returns from two-year-old plants of from 7 to 8cwt. per acre; these plants should be in full bearing next season, when it is hoped that improved yields and more reliable returns will be obtained. An account has been kept of the cost of production, and, while this presents difficulties when combined with experimental work, it is estimated that, apart from the wages of the foreman, the cost of production (1919-20) was approximately from £45 to £50 per acre. A yield of about 8 to 10cwt. of dried hops may be expected, and at (say) 3s. 6d. per lb. (£19 12s. per 112lb.) in South Africa, it would seem that from an economic point of view the prospects of remunerative hop-growing in well selected localities are worthy of consideration. There are still various points which will need to be investigated, and while it may now definitely be stated that hops can be grown satisfactorily in one part of South Africa, at any rate it is emphasised that the fringe only of what may possibly develop into a stable industry has been touched.

TITANIUM PEROXIDE.—Treatment of titanium sulphate with hydrogen peroxide gives a yellow solution, a base of which precipitates an amorphous yellow powder, $TiO_3$. In preparing the double sulphate of titanium and potassium, M. M. Billy separated the hydrate of peroxide and noted that all analogous bodies regarded as salts of the oxide $TiO_3$ are compounds of hydrogen peroxide and peritilanic salts corresponding to the peroxide $Ti_2O_5$.—*Comptes Rendus*, 1921.

BIOCHEMICAL PROCESS TO DETECT GLUCOSE.—The method of Bourquelot and Bridel is based upon the property of the emulsine to combine in an alcoholic medium, the sugar with the alcohol in which it is suspended. They endeavoured to apply the process to the study of plants and were thus able to obtain a characteristic $\beta$-methylgulcoside, the rotary power of which is easily determined and which, if in too small quantity, can be clearly seen under the microscope owng to the shape of its crystals.—*Comptes Rendus*, 1921.

ESSENCE OF JASMINE.—The flower of the jasmine is treated, in industry, to extract the perfume, by two very different methods, viz., that with volatile solvents (petroleum ether, rarely benzine), and secondly enfleurage, for which cold animal fats are utilised. Perfume manufacturers having noted since the employment of volatile solvents that the method styled enfleurage with cold animal fats gave a greater yield of perfume than with petroleum ether, M. Passy gives an explanation of this by the fact that in enfleurage the flowers continue to produce perfume owing to the vital activity of the cells and the quantity produced is only limited by survival of the flower. Thus, if it is killed by immersion in ether only, the perfume existing in the flower is obtained and production ceases with stoppage of the vital phenomenon. M. Passy proposes a method of enfleurage which consists in immersing the flowers

in water for a certain time. He extracted the essence by exhausting the water with ether. Resuming this idea, in a remarkable work, Mr. Hesse found that the yield from the jasmine in essence is five times greater with enfleurage than with volatile solvents. As the chemical composition of the essences obtained by the two processes is different, he supposes that there is a formation of odourous matter by decomposition of certain compounds, perhaps glucosides. Generalising this idea, Messrs. Charabot and Gatin regard it as a real chemical equilibrium: glucoside+water=glucose+essence. With this supposed decomposition of glucosides, the yield of essence could be increased by treating the jasmine flower so as to hydrolyse the glucoside or glucosides before extraction with petroleum ether. Experiment has demonstrated this to be so.—*Industrie Chimique*, June, 1921.

Quickly Drying Varnishes.—During the war, varnishes were utilised, which dried very rapidly (*Chem. Umschau in Neustr. Erfahr. und Erfind.* 1921, xxxviii., 3, 42). They were first made with wood oil and very high percentage of volatile solvents. They did not, however, dry quickly enough, and solutions of gum-lac were adopted (alcohol varnish). These also dried too slowly, and solutions of acetylcellulose were tried. For example, on can dissolve 550 grms. of cetylcellulose in 10 litres of a mixture of 60 parts methyl acetate, 10 methylethylcetone, 15 benzol, 10 acetone, 5 acetimic alcohol. To this solution 65 grms. of triphenyl phosphate are added, and sometimes small mixtures of phenyl acetate, benzyl benzoate, and urea. To make the varnish more elastic, 5 to 7 parts of castor oil are added, but the time of drying was increased. These varnishes were not used for airships, but gave washable coats for domestic work, especially on wooden partitions and wood floors. They were also employed as excipients for aluminium or zinc powder in metallic paints. They can be applied at a low temperature, and resist humidity. In many cases they are as good as oil varnishes.

## NEW COMPANIES.

The under-mentioned particulars of New Companies recently registered are taken from the Daily Register compiled by Jordan & Sons, Limited, Company Registration Agents, Chancery Lane, W.C.2.

E. R Cherrett, Limited.—(176157)—Registered August 8th, 1921. 18, Church Street, Monkwearmouth, Sunderland. To acquire and carry on the business of Chemists and Druggists. Nominal Capital. £3,000 in 3,000 Shares of £1 each. Directors: E. R. Cherrett, 6, Glenthorpe Avenue, Roker, Sunderland; N Jackson, 8, Campbell Terrace, Fulwell, Sunderland. Qualification of Directors · 100 Shares. Remuneration of Directors: E. R. Cherrett £7 10s. per week; N. Jackson £5 10s.

L. Dennis & Co., Limited.—(176182)—Registered August 9th, 1921. To carry on the business of Manufacturers of all kinds of Chemicals and Allied Products. Nominal Capital. £15,000 in 10,000 Preference Shares and 5,000 Ordinary Shares of £1 each. Directors · To be appointed by Subscribers. Qualification of Directors: £500. Remuneration of Directors · To be voted by Company in General Meeting. Subscribers L. Dennis, 26, Rutland Road, Walkden (Chemist); Kathleen Dennis, 26, Rutland Road, Walkden; W. Bannister, 19, Lawrence Road, Gledholt, Huddersfield.

P.L.A.C., Limited.—(176228)—Registered August 11th, 1921. 35, Walbrook, E.C.4. To acquire from Richard Pearson a process for the treatment of Acaroid Resins and the business of Manufacturing Acaroid Resins Lac. Nominal Capital: £400 in 400 Shares of £1 each. Directors: To be appointed by Subscribers. Qualification of Directors: 5 Shares. Remuneration of Directors: To be voted by Company in General Meeting.

## New Patents.

This List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W C.2, from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

20661—Bourcet, P.—Carburant for alcohol August 3
20758—Klages, A.—Process for production of aromatic cyan mercury compounds substituted in the core August 4.
20938—Pickard, H. F. K—Treatment of ores containing oxidized copper compounds August 6
20570—Reid, J. H.—Reduction of ore and production of gas. Aug 2.
20706—Ros, D.—Treating metallic sulphides August 2.
20583—Schuphans, G.—Method of producing chemically-pure hydrochloric acid. August 2.

*Specifications published this Week.*

140784—Soc anon—Produits Chemiques—Process for the production of acetaldehyde from acetylene.
166961—Clayton, T A.—Sulphur-burning furnaces
167066—Imray, O—Manufacture of aralkyl esters of 2 phenyl-quinonline-4-carboxylic acid

*Abstract Published this Week.*

*Phthalic Acid and Anhydride*—Patent No 164,785.—Messrs. The British Dyestuffs Corporation has obtained a Patent for an improved process for obtaining phthalic acid or its anhydride by treating naphthalene vapour with air or other oxygen-containing gas in the presence of a small amount of vanadyl chloride at 300-650° C. The mixture of naphthalene vapour, air, and vanadyl chloride vapour is passed through a vessel or tube, empty or containing pumice. fire-brick, kieselguhr, etc., and the products condensed in cooling chambers. In plate of naphthalene other volatile hydrocarbons or their derivatives yielding phthalic acid on oxidation, such as a- or B-methylnaphthalene, tetrahydronaphthalene, a-naphthol, or o-xylene, may be used.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

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THE CHEMICAL NEWS.

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# AN ANALYSIS OF MOLECULAR VOLUMES FROM THE POINT OF VIEW OF THE LEWIS-LANGMUIR THEORY OF MOLECULAR STRUCTURE.*

By ROBERT N. PEASE.

ACCORDING to the Lewis-Langmuir theory of valence and atomic and molecular structure (Lewis, *Journ. Am. Chem. Soc.*, 1916, xxxviii., 762; Langmuir, *ibid.*, 1919, xli., 868), the numbers of electrons surrounding the positive nuclei of the atoms of the inert gases are such as to permit of particularly stable arrangements. The atoms of the other elements enter into combination in such a manner as to group around their respective nuclei, by taking up, losing, or sharing electrons, a number of electrons equal to that in the atoms of the inert gas nearest to them in the periodic table. (It is not to the particular arrangements of electrons in the inert gases that the atoms of the other elements tend to revert, for in organic compounds, for example, the carbon atoms are assumed to have the 8 electrons arranged in pairs at the corners of a tetrahedron, while in neon, the corresponding rare gas, the 8 electrons are at the corners of a cube). As a result of this tendency, the number of electrons about the positive nuclei of atoms of those elements which tend to revert to the *same* rare gas is the same, when the atoms are in combination. Further, it sometimes happens that different atoms or groups of atoms, existing alone as molecules or acting as the nuclear atoms of compounds, have as a whole the same numbers and *arrangements* (this is always to be undestood to refer to all the electrons in the molecule or group of atoms, not merely to those in the outer shell) of electrons, and therefore differ only in the magnitude and distribution of the charges on the positive nuclei of the atoms. Such compounds and groups of atoms Langmuir (Langmuir, *Jour. Am. Chem. Soc.*, 1919, xli., 1543) calls "isosteres." Langmuir has pointed out the marked similarity of physical properties of pairs of isosteres which are capable of independent existence as molecules, such as nitrous oxide and carbon dioxide. This being the case, it does not seem improbable that the volumes of isosteric atoms or groups of atoms, whether these exist as free molecules or as the nuclear atoms of a compond, may be the same. This involves the assumption that the outer shells of electrons in isosteres have the same dimensions independent of the charges on the positive nuclei of the atoms or at least that the volume of the molecule as a whole shall behave as if this were the case (see note, *prox.*). The remainder of this paper is devoted to establishing the fundamental correctness of this assumption, and to examining the evidence furnished by molecular volumes regarding the structure of certain molecules and nuclear atoms.

For the comparisons of molecular volumes the values of the quantity $b$ of van der Waal's equation have been employed. These have been calculated from the relation $b={}_1/_8RT_c/p_c=0{\cdot}000458\ T_c/p_c$ in which, $T_c$ is the critical temperature in degrees, absolute; and $p_c$ is the critical pressure in atmospheres. The values of the critical temperature and pressure and of $b$ are given in Table I. The results of Young and the recent determinations of Cardoso have been used wherever possible.

TABLE I.—*The values of Critical Temperatures and Pressures, and of van der Waal's b.*

$T_c$ = critical temperature in degrees, Kelvin.
$p_c$ = critical pressure in atmospheres.
$b\times10^5=45{\cdot}8\ T_c/p_c$.

| | $T_c$ °K | $P_c$ Atmospheres | $b\times10^5$ | Observers |
|---|---|---|---|---|
| Ne | 44·7 | 26·9 | 76 | 14 |
| Ar | 150·7 | 48·0 | 144 | 8 |
| Kr | 210·5 | 54·3 | 177 | 17 |
| Xe | 289·7 | 58·2 | 228 | 15 |
| $H_2$ | 33·2 | 12·8 | 119 | 14 |
| $CH_4$ | 190·2 | 45·6 | 191 | 7 |
| $NH_3$ | 406·0 | 112·3 | 165 | 6 |
| $H_2O$ | 647·0 | 217·5 | 136 | 10 |
| $C_2H_4$ | 282·6 | 50·7 | 225 | 6 |
| $O_2$ | 155·0 | 49·3 | 144 | 7 |
| $C_2H_2$ | 308·6 | 61·7 | 229 | 6 |
| $N_2$ | 128·3 | 33·7 | 174 | 7 |
| CO | 134·4 | 34·6 | 178 | 7 |
| NO | 180·2 | 64·6 | 128 | 1 |
| $CO_2$ | 304·0 | 72·9 | 191 | 6 |
| $N_2O$ | 309·6 | 71·7 | 198 | 6 |
| $PH_3$ | 324·4 | 64·5 | 230 | 4 |
| $H_2S$ | 373·4 | 89·1 | 192 | 6 |
| HCl | 324·4 | 81·6 | 182 | 6 |
| $C_2H_6$ | 305·2 | 48·9 | 286 | 6 |
| $C_3H_8$ | 370 | 44·0 | 385 | 13 |
| $n$-$C_5H_{12}$ | 470·3 | 33·0 | 652 | 18 |
| $iso$-$C_5H_{12}$ | 460·9 | 32·9 | 641 | 18 |
| $n$-$C_6H_{14}$ | 507·9 | 29·6 | 785 | 18 |
| $n$-$C_7H_{16}$ | 539·9 | 26·9 | 919 | 18 |
| $n$-$C_8H_{18}$ | 569·3 | 24·6 | 1057 | 18 |
| $(CH_3)_2CH.CH(CH_3)_2$ | 500·5 | 30·7 | 745 | 18 |
| $(CH_3)_2CHCH_2CH_2CH(CH_3)_2$ | 549·9 | 24·6 | 1025 | 18 |
| $(CH_3)_2O$ | 400·1 | 53·0 | 346 | 5 |
| $(C_2H_5)_2O$ | 466·9 | 35·6 | 600 | 18 |
| $C_2H_5NH_2$ | 456·2 | 55·5 | 376 | 3 |
| $(CH_3)_2NH$ | 437·6 | 52·4 | 382 | 3 |
| $(C_2H_5)_2NH$ | 496·3 | 36·6 | 621 | 3 |
| $Cl_2$ | 414·0 | 83·9 | 226 | 9 |
| | 419·0 | 93·5 | 205 | 11 |
| | 417·0 | 76·1 | 252 | 16 |
| $CCl_4$ | 556·2 | 45·0 | 566 | 18 |
| $GeCl_4$ | 550·0 | 38·0 | 663 | 12 |
| $SnCl_4$ | 591·8 | 37·0 | 733 | 18 |
| $C_6H_6$ | 561·6 | 47·9 | 537 | 18 |
| $C_6H_{12}$ | 553·1 | 39·8 | 635 | 18 |
| $C_6H_5CH_3$ | 593·7 | 41·6 | 653 | 2 |
| $C_6H_5F$ | 559·6 | 44·6 | 574 | 18 |
| $C_6H_5Cl$ | 632·3 | 44·6 | 648 | 18 |
| $C_6H_5Br$ | 670·0 | 44·6 | 687a | 18 |
| $C_6H_5I$ | 721·0 | 44·6 | 740a | |

*a* Calculated by Young.

1. Adwentowski, *Ion*, 1910, ii., 1; cf. *C.A.*, 1910, iv., 2777.
2. Altschuel, *Z. physik. Chem.*, 1893, xi., 577.
3. Berthoud, *J. chim. phys.*, 1917, xv., 3.
4. Briner, *ibid.*, 1906, iv., 476.
5. Briner and Cardoso, *ibid.*, 1908, vi., 641.
6. Cardoso, *J. chim. phys.*, 1912, x., 470.
7. Cardoso, *ibid.*, 1915, xiii., 312.

* From *Journal of American Chemical Society*, May, 1921.

8. Crommelin, *Comm. Phys. Lab. Leiden*, 1910, cxv., 118
9. Dewar, *Phil. Mag.*, 1884, [5] xviii., 210.
10. Holborn and Baumann, *Ann. Phys.*, 1910, [4] xxxi., 945.
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12. Nilson and Pettersson, *Z. physik. Chem.*, 1887, i., 38.
13. Olszewski, *Phil. Mag.*, 1895, [5] xxxix., 188.
14. Onnes, *Proc. Acad. Sci Amsterdam*, 1917. xx., 178.
15. Patterson, Cripps, and Whytlaw Gray, *Proc. Roy. Soc.*, [*A*], 1912, lxxxvi., 579.
16. Pellaton, *J. chim. phys.*, 1915, xiii., 426
17. Ramsay and Travers, *Phil. Trans. Roy. Soc.*, 1901, cxcvii., 47.
18. Young, *Sci. Proc. Roy. Dublin Soc.*, 1909-10, N.S. xii., 374.

Unfortunately, lack of space does not permit an extended discussion of the recent paper of J. J. Van Laar (Van Laar, *J. chim. phys.*, 1916, xiv., 3) on the addivity of the quantity *b* of van der Waal's equation. He has assumed arbitrary and sometimes variable values for the volumes of the atoms and obtains good average agreement between calculated and observed values. His atomic volumes are, however, difficult to reconcile with the Lewis-Langmuir theory.

The paragraphs immediately following deal with the molecular volumes of those compounds which contain carbon, nitrogen, and oxygen as nuclear atoms.

*Methane, Ammonia, and Water.*—The nuclear carbon, nitrogen, and oxygen atoms in methane, ammonia, and water respectively, are isosteric, since each consists of a positive nucleus and pair of electrons surrounded by an octet of electrons If these isosteric nuclear atoms have the same volume, then the differences in volume between pairs of these substances will be the volume of the extra hydrogen atoms one contains over the other. The volumes of the compounds are: methane, 191; ammonia, 165; water, 136. Methane has one more hydrogen than ammonia, and is greater by 26 units. Ammonia has one more hydrogen than water, and is greater by 29 units. It should be remembered that the errors in the volumes fall on these differences Taking the average difference of 28 as the volume of one hydrogen atom in these compounds, and subtracting for the total number of hydrogen atoms from the volume of each compound, to find the volumes of the nuclear atoms, one obtains for the latter the values

$CH_4$: 191-112=79
$NH_3$: 165-84 =81 Average 80.
$H_2O$: 136-56 =80

The nuclear atoms are seen to have almost exactly equal volumes, substantiating the assumption made.

For neon, the corresponding inert gas, the volume is 76. That the volume of the nuclear atoms in the above compounds is practically the same (80) would seem to indicate that these atoms are essentially cubic, as neon is assumed to be. The tendency of the hydrogen atoms to draw together the pairs of electrons, by means of which they are held, to give the nuclear atom a tetrahedral structure, is apparently not great. That the volume of the nuclear atoms and that of neon are not more nearly equal may be due to slight deformation of the cubic structures in the hydrides or to the inaccuracy of the value for neon, the critical data for which are given by Kammerlingh Onnes as preliminary.

*Ethylene and Oxygen.*—Elementary oxygen and the carbon atoms in ethylene are isosteric. In both, the positive nuclei (with a pair of electrons each )are surrounded by 12 electrons forming two tetrahedral octets sharing two pairs, that is, meeting along an edge If the volumes of the two isosteres are the same, the difference in volume between ethylene (255) and oxygen (144) represents the volume of the four hydrogen atoms in ethylene. One-fourth of this difference should be the volume of one hydrogen.

$$\frac{V_{C_2H_4} - V_{O_2}}{4} = \frac{255 - 144}{4} = 28$$

The volume of one hydrogen is found to be 28 as in methane and the like.

*Acetylene, Nitrogen, and Carbon Monoxide.*—For reasons to be discussed later, nitrogen and carbon monoxide are assumed to have the normal, acetylenic, arather than the condensed structure suggested by Langmuir. Thus, nitrogen, carbon monoxide, and the carbon atoms of acetylene are isosteric, since the structure for all consists of two positive nuclei (with a pair of electrons each) surrounded by two tetrahedral octets composed of 10 electrons, three pairs being shared, that is, meeting face to face.

The volumes of nitrogen and carbon monoxide are 174 and 178, respectively, that of the unsymmetrical carbon monoxide being slightly the greater. Taking symmetrical nitrogen to compare with the symmetrical carbon atoms of acetylene (229), it is found that one-half the difference between the volumes of the two compounds, which should equal the volume of one hydrogen atom, is again 28.

$$\frac{V_{C_2H_2} - V_{N_2}}{2} = \frac{229 - 174}{2} = 28$$

It is convenient to point out here that the volumes of carbon dioxide and nitrous oxide, which are isosteric, are 191 and 198 respectively. If nitrous oxide has the structure N=N=O, as Langmuir is inclined to think, then again the unsymmetrical isostere ($N_2O$) has slightly the greater volume, as found in comparing carbon monoxide and nitrogen. The lack of symmetry in both cases is in the distribution of positive charge among the nuclei of the atoms.

Elementary fluorine is isosteric with the nuclear carbon atoms of ethane. As, however, the critical constants of the former have not been determined, no comparison can be made. It will be of interest to obtain a value for two tetrahedral neon octets sharing one pair, as in ethane. This can be done by subtracting 6×28 for 6 hydrogens from the value for ethane (286); thus 286−168=118 for the nuclear C—C atoms.

*Summary.*—From the above it results that with one value (28) for hydrogen, 80 for the cubic neon structure, 144 for two tetrahedral neon structures sharing two pairs and 174 when sharing three pairs, the volumes of methane, ammonia, water, ethylene, acetylene, carbon monoxide, oxygen and nitrogen can be reproduced as follows.

| | Observed. | Calculated. | Δ | Van Laar calc | Δ |
|---|---|---|---|---|---|
| $CH_4$ | 191 | 192 | +1 | 156 | −35 |
| $NH_3$ | 165 | 164 | −1 | 162 | −3 |
| $H_2O$ | 136 | 136 | 0 | 138 | +2 |
| $O_2$ | 144 | (144)*a* | ... | 140 | −4 |
| $C_2H_4$ | 255 | 256 | +1 | 256 | −1 |
| $N_2$ | 174 | (174)*a* | ... | 170 | −4 |
| $C_2H_2$ | 229 | 230 | +1 | 228 | −1 |
| CO | 178 | 174 | −4 | 170 | −8 |

*a* Assumed in the calculation.

The calculated values agree with the observed within 0·5 per cent with the exception of that for carbon monoxide, which is about 2 per cent too low.

The results obtained in the foregoing analysis are taken to be good evidence of the correctness of the assumption that isosteres, whether existing alone as molecules or forming the nuclear atoms of hydrides have the same volume, independent of the particular atoms involved. It is very unlikely that all the relations cited above—namely, that the volumes of methane, ammonia, and water can be expressed with one value for all the nuclear atoms and another for hydrogen, or that this same value for hydrogen and the values for elementary oxygen and nitrogen can express the volumes of ethylene and acetylene, respectively—are simply fortuitous. It is true that Van Laar, making different assumptions, finds nearly as good agreement, with the exception of his value for methane, which is seriously in error (156 calculated; 191 observed). In order to get this agreement, however, he requires two values for hydrogen, two for nitrogen, and one each for carbon and oxygen. In the present analysis, one value is used for hydrogen, and three different values are assigned to the three different arrangements of electrons about the neuclear atoms met with in these compounds.

*Effect of Multiple Bonds.*—For ethane, ethylene, and acetylene, Van Laar uses a single value each for carbon and hydrogen, in effect assuming that the differences in volume among these compounds depend wholly upon the number of hydrogen atoms in the different molecules. The results recorded in this paper indicate that there is, in addition, a difference due to the manner in which the carbon atoms are combined, that is to say, a difference due to the type of electron structure. Expressed in terms of the volume of a single atom, the values for a single neon octet combined in the various ways are: sharing no pairs ($CH_4$, etc.) 80; sharing one pair ($C_2H_6$) 59 (118/2); sharing two pairs ($O_2$ and $C_2H_4$) 72 (144/2); sharing three pairs ($N_2$ and $C_2H_2$) 87 (174/2).

When one pair is shared, the volume is one-quarter less (59/80=74 per cent) than when no pairs are shared. The similarity between the volumes of the nuclear atoms in methane, &c. (when no pairs are shared with other octets) and that of neon was taken to indicate that the nuclear atoms in the former are nearly cubic. In ethane, the nuclear atoms are almost certainly tetrahedral. The ratio of the volumes probably represents, therefore, the relation between the volumes of the cubic octet and the tetrahedral octet of neon.

When two pairs are shared, the volume of a single atom is 13 units greater than when one pair is shared, and when three pairs are shared, there is a further increase of 15 units per atom. The distances between the centres of two tetrahedra meeting (*a*) at their apexes (*b*) along an edge (*c*) at a face, are in the ratio, 4 : 3 : 2. These configurations correspond to the sharing of one, two, and three pairs, respectively. Thus, the tendency if unresisted, on sharing two and three pairs would be to bring the positive nuclei at the centres of the tetrahedral electron shells nearer and nearer together. The volume increases on sharing successively the second and third pairs represent the reaction of the positive nuclei against this tendency. By attempting to get as far apart as possible, they distend the molecule. This state of tension due to the multiple bond is evidently an element of weakness and the multiple bond might be expected to be a seat of chemical activity, as is known to be the case.

*Structure of Nitrogen.*—Langmuir accounts for the inertness of nitrogen and carbon monoxide by assuming a condensed structure consisting of the two positive nuclei each holding a pair of electrons (correspondng to helium) and holding between them a third pair, this structure being surrounded by eight electrons at the corners of a cube. The alternative structure consists of two octets sharing three pairs, as do the carbon atoms in acetylene. As the reactivities of nitrogen and carbon monoxide are not so great as that of acetylene, Langmuir is inclined to think the structures cannot be similar. Reactivity is, however, a rather vague term. It is true that nitrogen is commonly spoken of as inert, and acetylene as active chemically. Yet if the strength of the bond joining the the nuclear atoms be measured by the tendency of the two compounds to dissociate, the one into nitrogen atoms and the other into CH radicals, the *stabilities* must certainly be assumed to be of the same order.

As pointed out in the first part of this paper, there is good evidence that the volumes of elementary nitrogen and the two carbon atoms of acetylene are the same, thus indicating a similarity in structure. Furthermore, one would expect such a very condensed structure as Langmuir suggests for nitrogen, the outermost electrons of which form only a single octet, to have a decidedly smaller volume than elementary oxygen, for example, the outer shell of which consists of two octets of electrons sharing two pairs; or of argon, which consists of a single positive nucleus (but with a positive charge of 18), a pair of electrons and two octets of electrons one outside the other. Actually, the volumes of elementary oxygen and of argon are both 144, while that of elementary nitrogen—174—is decidedly larger than either.

The fact that the volume of elementary nitrogen is greater than that of elementary oxygen also has a bearing on the general assumption made in this paper, that it is principally the particular arrangement of electrons rather than the charge on the positive nuclei which determines the volume of an atom or group of atoms. Since the positive nuclei of oxygen atoms posses a charge of +8, while that of the nitrogen atoms is +7, one might have expected that the greater repulsion between the larger nuclei of oxygen would have given to elementary oxygen the greater volume. That it is distinctly less in volume than is elementary nitrogen, with +7 positive nuclei, indicates that the volume is more influenced by other factors. The other apparent difference between the compounds, according to the theory, being in

the number and arrangement of the electrons—the limiting boundaries of the molecules—it is reasonable to refer the volume relation rather to this.

*Nitric Oxide.*—Nitric oxide is peculiar in having an odd number of electrons (15). It is thus intermediate between elementary nitrogen with 14, and elementary oxygen with 16 electrons. Langmuir has suggested that it may have essentially the structure which he assigns to elementary nitrogen, the extra, odd electron being "imprisoned in the octet comprising the shell." As this structure for nitrogen has been rendered doubtful by the preceding considerations it will be of interest to find what other structure is possible and what are the indications furnished by the volume of the substance.

The volume of nitric oxide is suprisingly small, 128, that of oxygen being 144, and nitrogen, 174. It is, in fact, actually nearer that of the carbon atoms in ethane (118). Nitric oxide contains one more electron than nitrogen, and it is possible that in the former the octets, like those in nitrogen, share three pairs, the odd electron being at the centre of the triangle formed by these three pairs, directly between the two positive nuclei and held in place by the attraction of the latter The odd electron so placed would certainly tend to draw the nuclei together, lessening the distention of the molecule and making the volume of the molecule less than that of elementary nitrogen. Actually the volume is reduced nearly to the normal volume of two octets sharing a single pair as exemplified by the carbon atoms in ethane. In the latter case, the shared electron pair is also placed directly between the two positive nuclei.

The odd electron, place as suggested above, would certainly be held under rigid constraints. Lewis (*loc. cit.*), who would attribute colour in compounds to weakly-held electrons, has pointed out that of the substances containing an odd number of electrons, only nitric oxide is colourless, that it to say, all the electrons including the odd, are rigidly held.

*Hydrocarbons, Amines, and Ethers.*—There are a few hydrocarbons, amines, and ethers for which data are available whose chains of nuclear atoms are isosteric and should, therefore, have equal volumes. A comparison of the 5- and 3-atom chains is given below. The volumes of the chains have been obtained by subtracting 28 for each hydrogen atom from the volumes of the compounds. It should be borne in mind that this method throws all the experimental error on the volume of the chain.

*5-Atom Chains.*

| | $b \times 10^5$. 28 H. Chain. |
|---|---|
| $n$-$C_5H_{12}$ | 652−336=316 |
| $(C_2H_5)_2NH$ | 621−308=313 |
| $(C_2H_5)_2O$ | 600−280=320 |

*3-Atom Chains.*

| | $b \times 10$ 28 H Chain. |
|---|---|
| $C_3H_8$ | 385−224=161 |
| $C_2H_5NH_2$ | 376−196=180 |
| $(CH_3)_2NH$ | 382−196=186 |
| $(CH_3)_2O$ | 346−168=178 |

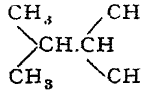
With the exception of the value obtained from propane, the agreement is satisfactory within each series.

*Hydrocarbon Chains.*—As is well-known, the volumes of compounds containing long chains of carbon atoms are not strictly additive. The values for the increment $CH_2$ usually rise in ascending a series. This is true of the values of $b$ for the straight-chain hydrocarbons, as will be seen from the following comparison of observed values with those calculated from the values H=28 and C=59 (as found in ethane).

| | Observed | Calc. | | Per cent. |
|---|---|---|---|---|
| $C_2H_6$ | 286 | (286) | ... | ... |
| $C_3H_8$ | 385 | 401 | 16 | 4·2 |
| $n$-$C_5H_{12}$ | 652 | 631 | 21 | 3·2 |
| $n$-$C_6H_{14}$ | 785 | 746 | 39 | 5·0 |
| $n$-$C_7H_{16}$ | 919 | 861 | 58 | 6·3 |
| $n$-$C_8H_{18}$ | 1057 | 976 | 81 | 7·7 |
| $(CH_3)_2CH.CH_2CH_3$ | 641 | 631 | 10 | 1·6 |
| $(CH_3)_2CH.CH(CH_3)_2$ | 745 | 746 | 1 | 0·1 |
| $(CH_3)_2CH.CH_2CH_2CH(CH_3)_2$ | 1025 | 976 | 49 | 4·8 |

For the straight chain compounds, the percentage by which the observed values exceed the calculated steadily increases, with increasing number of atoms.

The branched chain isomers have volumes smaller than the straight chain, and therefore nearer the calculated values. It is of interest to note that that compound in which the relative amount of departure from the straight chain is greatest, namely, di-*iso*-propyl,



has a volume almost identical with that calculated (745 observed; 746 calculated).

*Ring Structures.*—It is of interest to find what values are obtained for ring structures. The value for toluene will first be examned. The radical, $C_6H_5$, should have a volume equal to that of benzene less one hydrogen atom or 537−28=509. The volume of $CH_3$ should be $59+(3\times28)=143$. The sum of these gives the value for toluene, $C_6H_5CH_3$, 652. The observed value is 653.

For the rings in benzene and cyclohexane, the following values are obtained by subtracting for the total number of hydrogen atoms: $C_6H_6$, $537-(6\times28)=369$; $C_6H_{12}$, $635-(12\times28)=299$.

The unsaturated benzene ring has the greater volume. This is in agreement with the relations already found between the volumes of saturated and unsaturated nuclear atoms. The carbon atoms in cyclohexane might have been expected to have the volume 59 each. Actually the volume is 299/6=50. The ring structure appears to be very much condensed.

*Phosphine and Hydrogen Sulphide.*—Data are not available for enough compounds having nuclear atoms related to argon, as those just discussed are related to neon, to allow very satisfactory comparisons to be made. There are dependable values for phosphine, hydrogen sulphide and hydrogen chloride, however, and these will be analysed so far as possible.

If, as in the case of methane, ammonia, and water, the difference between the volumes of phosphine and hydrogen sulphide (230−192=38) be taken as the volume of one hydrogen in these substances, then for the volume of the nuclear atoms, one obtains: $PH_3$, $230-(3\times38)=116$; $H_2S$, $192-(2\times38)=116$. Because of the method of treatment the value for the nuclear atom is necessarily the same in both cases This value (116) is 116/144,

or 80 per cent of that of the corresponding rare gas, argon. A carbon atom in ethane sharing one pair (and in the tetrahedral form) has a volume 59/76, or 78 per cent of that of the corresponding cubical atom, neon. As the volumes of the nuclear atoms in phosphine and hydrogen sulphide bear nearly the same numerical relation to that of the corresponding cubic atom, argon, it would appear that already in the simple hydrides the nuclear atoms related to argon are tetrahedral. The hydrogen atoms by their attraction for pairs of electrons appear to have been able to deform the argon (cubic) structure to such an extent that it is essentially tetrahedral. As the volume of argon is nearly twice that of neon (144, 76) one might have expected this relatively greater deformation of the former structure.

*Volume of Hydrogen.*—The volume of hydrogen in these compounds appears to be greater than in those compounds containing nuclear atoms related to neon. This is undoubtedly the effect of the very much larger charge on the positive nuclei of atoms related to argon. The hydrogen atom in each of these compounds actually consists only of a singly charged positive nucleus of exceedingly small volume held by means of an electron pair of the nuclear atom but repelled by its positive nucleus. Its contribution to the volume therefore, depends on the equilibrium position it holds with respect to the electron pair and positive nucleus of the nuclear atom. If it is forced out, its apparent volume will be greater and *vice versa*. The hydrogen atom cannot be expected therefore, to have a constant volume. This is emphasised by the fact that in the elementary state ($b = 119 \times 10^{-5}$), the atom has the relatively very great volume of 60. The greater apparent volume of hydrogen in hydrogen sulphide as contrasted with that in water is indicative of the greater ease of ionisation of the former compound —the hydrogen nucleus is normally separated from the nuclear atom to a greater extent It may be pointed out here that Van Laar's values of 14 for hydrogen combined with carbon and 34 for hydrogen combined with any other atom, are not so easily explained. Although carbon is a very peculiar element, it is not so markedly different from all other elements, on the basis of the theory, as to lead one to expect any such distinction between the volume of hydrogen associated with it and associated with any other element. One would rather expect either a different value for hydrogen combined with each element or compound, increasing with increasing atomic weight of the element or else for each rare gas type of nuclear atom, as apparently is the case. (It is possible that the apparent volume of the hydrogen atom does increase slightly as the charge on the positive nucleus of the nuclear atom increases, but that this is offset by the fact that the electron shell about the nuclear atom *decreases* slightly in volume with increasing nuclear change—the electrons are displaced inward somewhat. It is, in fact, possible to get slightly better agreement assuming a slight regular increase in volume for hydrogen and decrease in volume for the nuclear atom with increase in charge on the positive nucleus of the nuclear atom, in any given series).

*Hydrogen Chloride.*—The treament of the value for hydrogen chloride presents certain difficulties. One is prepared to find a structure rather different fro many of those so far considered, because of the strongly polar nature of the compound. The value (182) is clearly relatively greater than that of hydrogen sulphide, since with one less hydrogen, the value is only 10 less (192, 182). If 38, the value for hydrogen in phosphine and hydrogen sulphide be subtracted from the hydrogen chloride value, the remainder ($182 - 38 = 144$) is precisely the value of argon itself. The chlorine atom in hydrogen chloride thus appears to have the cubic structure, one hydrogen being insufficient to force the atom into the tetrahedral form. This is, of course, juse the form (*i.e*, cubic) which the halogen and alkali atoms are supposed to have in alkali halide crystals, the alkali halides being also highly polar. The assumption of the cubic argon structure by the chlorine atom in hydrogen chloride may serve in some degree to account for the difference in properties between hydrogen chloride and hydrogen sulphide.

*Chlorine.*—The various determinations of the critical constants for elementary chlorine are, unfortunately, widely divergent. The values for $b \times 10^{+5}$ are 226 (Dewar) 205 (Knietsch, 1890) and 252 (Pellaton, 1915), giving the values 113, 103, and 126 for one chlorine atom. Van Laar chooses to take Dewar's value (113), which is not far from that found here for the nuclear atoms in phosphine and hydrogen sulphide (116). The latter were assumed to be more nearly tetrahedral. Two octets sharing one pair with no combined hydrogen atoms may not be tetrahedral, however. Undoubtedly the attraction of the two positive nuclei will tend to draw the shared electrons toward the line joining the nuclei, thus deforming the cubic structure, and the volume of the molecule will at least be less than that of two cubic structures with volume 144 (argon) each. Pellaton's recent value of 126 for each atom in elementary chlorine seems best to fulfil the requirements, since it is midway between that of the tetrahedral atoms in phosphine and hydrogen sulphide (116), and that of the cubic atom, argon (144), corresponding to a deformed cube structure.

*Atoms Similar to Krypton and Xenon.*—It is not possible to make an analysis of the volumes of compounds containing nuclear atoms related to krypton and xenon, because critical data have only been determined for one or two. Since, according to Langmuir, the outer shell of these atoms is made up of 18 instead of 8 electrons, one cannot apply the results already arrived at to the examination of these few compounds. There are, however, two series of compounds the volumes of which yield interesting results. These are the tetrachlorides of carbon, germanium and tin and fluoro-, chloro-, bromo-, and iodobenzene.

*The Tetrachlorides of Carbon, Germanium, and Tin.*—If the carbon atom in carbon tetrachloride (566) be taken to be tetrahedral (59), as it almost certainly is, since it shares all four pairs, there is obtained for the volume of one chlorine ($(566 - 59/4 = 127$). This is very close to Pellaton's recent value for one chlorine atom in elementary chlorine (126). If 127 be taken as the volume of one chlorine in germanium and tin tetrachlorides, one obtains for the volume of germanium and tin $GeCl_4$, $663 - 507 = 156 = Ge$; $SnCl_4$, $733 - 507 = 226 = Sn$. The volumes of the corresponding rare gases

are krypton, 177, and xenon, 228. The value for tin (226) is close to that of the corresponding rare gas, xenon (228), indicating that the shell of 18 electrons has not been greatly deformed. As the electrons are probably closer together than in the shell of chlorine, it is not impossible that the chlorine might be deformed cubic and the tin atom still have essentially the structure of the rare gas, xenon. The value for germanium (156) is somewhat less than that of the rare gas, krypton (177), to which it corresponds. This would seem to indicate some deformation. However, of the two, greater weight must be attached to the value for tin, since the constants for tin tetrachloride are those of Young, while the constants of germanium tetrachloride were determined by Nilson and Petterson (1887) and represent, so far as known, the only determinations of critical constants published by these authors.

A new determination of the critical constants of germanium tetrachloride and a determination of those of silicon tetrachloride would be of great value in this connection.

*The Aromatic Halogen Compounds.*—The value for benzene is 537. Subtracting 28 for one hydrogen, the value 537−28=509 is obtained for the phenyl radical, $C_6H_5$. If this value be subtracted from those of the aromatic halogen compounds, the remainder should be the volume of the halogens: $C_6H_5F$, 574−509=65=F; $C_6H_5Cl$, 648−509=139=Cl; $C_6H_5Br$, 687−509=178=Br; $C_6H_5I$, 740−509=231=I.

For fluorine, a value between 59 (tetrahedral) and 80 (cubic) was to have been expected. The value found is 65. For chlorine, the value 126 was looked for. Actually a value (139) somewhat nearer that of argon (144) was obtained. For bromine (178) and iodine (231), values close to those of the corresponding rare gases, krypton (177) and xenon (228) are obtained, as in the case of tin in tin tetrachloride. As bromine and iodine each share with the radical only one pair out of 18 electrons, one would certainly not expect any great deformation, and little apparently occurs.

*Volumes of the Rare Gases.*—According to Langmuir (*Jour. Am. Chem. Soc.*, 1919, xli., 932), "the electrons in *any given atom* are distributed through a series of concentric shells, all of equal thickness. Thus, the mean radii of the shells form an arithmetic series, 1, 2, 3, 4 . . . ." These shells contain two sets of electrons. Thus, in xenon, the first shell contains the two electrons corresponding to helium, the second shell contains the two octets of electrons corresponding to the outermost electrons of neon and argon, respectively, and the third shell contains the two sets of 18 electrons, one outside the other, corresponding to the outermost electrons of krypton, and finally, xenon itself. It is specifically stated that this relation of the radii of the shells holds only for one given atom. It will, however, be of interest to see if any such simple relation holds for different atoms.

If the radii are in the ratio 1 : 2 : 3, the mean volumes of the shells must be as 1 : 8 : 27. If the mean volume of a given shell is the same in every atom which contains it, then it might be expected that the mean of the volumes of neon and argon, representing the second shell (helium accounts for the first) and of krypton and xenon, representing the third shell, would be to each other as 8 : 27. The values actually obtained are (76+144)/2=110; and (177+228)/2=202·5. The mean of the volumes of neon and argon is 110, that of krypton and xenon, 202·5. These are clearly not in the ratio required. In krypton and xenon, it is quite possible that because of the larger charge on the positive nucleus, the electrons of the second shell will be drawn inward more than the corresponding electrons in neon and argon, and the mean volume of the shell be enough smaller than in neon and argon to satisfy the relation. (It is of interest to note that the volumes of the rare gases are roughly proportional to the square roots of their atomic weights, as will be seen from the following Table:—

| | $b$ | At. wt. | $\sqrt{\text{At. wt.}}$ | $\frac{b}{\sqrt{\text{At. wt.}}}$ |
|---|---|---|---|---|
| Ne . . .. . . | 76 | 20 | 4·47 | 17·0 |
| A ... .. ... | 144 | 40 | 6·32 | 22·8 |
| Kr ... ... .. | 177 | 83 | 9·11 | 19·4 |
| Xe ... ... ... | 228 | 130 | 11·4 | 20·0 |

In fact, rough average agreement can be obtained for molecular volumes (in general) if they are assumed to be proportional to the sum of the square roots of the atomic weights of the constituent atoms).

Two facts in particular, are brought out by the foregoing analysis. First, isosteric atoms, molecules and groups appear to have the same volume regardless of the particular kinds of atoms of which they are composed. In other words, the number and arrangement of electrons in the outer shells of atoms or groups of atoms is the predominating factor in determining their volume. Second, the volumes of other atoms, particularly of the more complex ones, are intimately related to the volumes of the rare gases.

It is realised that the possibilities of the method of treatment used in this paper are by no means exhausted, and the writer expects at some future time to consider further the implications of the present work.

*Summary.*

1. An analysis of molecular volumes, as determined from the critical data, has been made from the point of view of the Lewis-Langmuir theory, and especially of Langmuir's theory of isosteres.

2. Evidence has been brought forward to show that isosteric molecules and nuclear atoms in hydrogen compounds have the same volume. The volume depends, therefore, on the number and arrangement of electrons surrounding the positive nuclei of the atoms rather than on the charges on the nuclei, that is to say, on the particular kinds of atoms concerned. Thus, it has been shown that the nuclear carbon, nitrogen, and oxygen atoms of methane, ammonia, and water, respectively, have the same volume.

3. It has been shown that the carbon atoms in ethane, ethylene, and acetylene have volumes increasing with the degree of unsaturation. The same observation holds in comparing the carbon atoms in benzene and cyclohexane. The volumes of atoms thus increase with the number of electron pairs shared. An explanation of this has been presented.

4. It has been shown that elementary nitrogen and carbon monoxide probably have the normal or acetylenic structure, three pairs being shared, rather than the condensed structure suggested by Langmuir.

5. A structure for nitric oxide has been suggested and evidence in its favour produced.

6. The volumes of the rare gases have been considered from the point of view of Langmuir.

The writer is especially indebted to Professors H. S. Taylor and Alan W. C. Menzies for criticism and suggestions regarding the work summarised in this paper.

## THE BLEACHING OF SHELLAC.

By S. T. GADRE.

THE action of sunlight can decolorise a solution of shellac as well as can animal charcoal. Shellac can also be deprived of its colour by pouring its alcoholic solution into potassium hypochlorite solution or by passing chlorine into a potash solution of shellac. But these methods do not find commercial application.

*Theory of the Process.*—Bleached shellac is prepared from ordinary shellac by the action of hypochlorite of soda on the alkaline solution for the purpose of removing the red-brown colour of the lac. The lac dye is bleached very quickly, but the yellow colour of the erythrolaccin is more persistent, and a greater or smaller quantity survives the bleaching entirely; hence the bleaching is due to the more or less complete destruction of the erythrolaccin.

*Description of Process.*—The method employed for bleaching shellac was as follows: 1lb. of soda ash was dissolved in 3 gallons of water and heated to boiling point in a circular wooden vat fitted with lead piping for steam heating. 5½lb. of ground shellac (button lac) were then added slowly. The shellac dissolved in the alkaline solution, leaving only a small amount of suspended matter (impurities floating) on the surface. 5½lb. of bleaching powder were then dissolved in 10½ gallons of water: to this mixture 4½lb. of soda-ash were added. The whole was well stirred and filtered. The clear solution so obtained is sodium hypochlorite. This solution was then added to the hot shellac solution. The addition was effected gradually, and in small portions towards the end, with short intervals between the additions.

*Characteristics of the Product Obtained.*—The product obtained by bleaching shellac is white in appearance, and is rather crisp and brittle. Bleached shellac in the form of a dry powder is ready for immediate use for the preparation of shellac varnish, this variety being largely employed in the United States. Bleached shellac contains no wax but still contains water, and gradually undergoes a change into a modification insoluble in alcohol and alkalies. This change cannot be prevented. It will take place with greater ease at high temperatures. Bleached shellac should be used promptly. It dissolves in the same solvent as orange shellac: the solution is milky white, (the milkiness being due to the suspension of insoluble shellac wax. In alcoholic shellac solutions, the wax partly settles in time. Bleached shellac should be stored in as cool a place as possible, and should be kept under water. This precaution is necessary to avoid blocking of shellac in summer weather.

The samples of bleached shellac obtained in this laboratory were examined, firstly, with a sample of bleached shellac from England, and secondly, with a sample manufactured by Messrs. D. Waldie & Co., Konnagar. Table I. gives comparative results. The solubility figures show the enormous deterioration which bleached shellac undergoes on exposure to light and air:—

The materials used in the experiment analysed as follows:—

1. Button lac (shellac). Iodine value, 3·01 (by Wij's solution). (Allowable limit of iodine value for T.N. shellac, 14—17. Iodine value increases as perecentage of resin in shellac increases. Shows freedom from resin).
2. Soda-ash, 85 per cent $Na_2CO_3$.
3. Bleaching-powder contains 25 per cent available chlorine on an average.

*Calculation of Costs of Experiments as carried out.*

| Shellac (button lac). | Rs. | a. | p. |
|---|---|---|---|
| 5½lb. at Rs.275 per maund ... ... ... | 18 | 6 | 0 |
| Soda-ash 5½lb. at Rs.6-8-0 per cwt. ... | 0 | 5 | 3 |
| Bleaching-powder 5½lb. at Rs.71 per cwt. | 3 | 8 | 0 |
| *Steam ... ... ... ... ... ... ... | Negligible | | |
| Labour—one workman at 8 annas a day for an 8-hour day ... ... ... ... | 0 | 8 | 0 |
| | 22 | 11 | 3 |
| | Or, say, Rs.23 | | |

* The very small amount of steam used is only a very minute fraction of that required in the works for pumping water and for other purposes.

Taking the yield of bleached shellac as 5½lb. less 0·22lb., or 4 per cent less (3 per cent being lac wax and 1 per cent insoluble matter) or 5·28lb, the cost of production per lb. of bleached shellac works out at Rs.4-6-0. The cost will be very greatly reduced if the production of large quantities of bleached shellac is taken in hand, and also if cheap chlorine be made available in quantity.

TABLE I.

| Sample of bleached shellac. | Colour. | Hardness. | Solibility in cold alcohol (62·5 per cent.) |
|---|---|---|---|
| *English make | White (very slightly dark at the core). | Very crisp | 12·1 per cent soluble |
| **D. Waldie's make | Dark | Rather plastic | |
| †Our own make | White | Crisp | 56·6 per cent soluble |
| ‡Our own make | White | Rather plastic | Almost complete |

* The sample had been kept in our laboratory for a long time.
** The shellac was stored under a slightly acid solution.
† Kept exposed to light and air for six months.

The calculation has been made with inflated prices of shellac and bleaching powder, such as are current at the present time. In 1903-4 the price of shellac rose to 230s. per cwt.; in 1908-9 the price was reduced to 60s. per cwt. Quite exceptional prices were reached during the war, even 400s. per cwt. being exceeded. In 1918, arrangements had been made in England by which the shellac required for munitions was obtained direct from India at 144s. 6d. per cwt for all Government contractors who could produce evidence that they required the supplies for Government orders.

*Composition of Bleached Shellac.*—According to Tschirch, bleached shellac contains chlorine, so that the iodine absorption is materially modified. Fraymouth ("An Argument for a Change in the Lac Industry," Indian Munitions Board Industrial Handbook, 1919) says that an additive compound of shellac with chlorine is obtained.

This problem will shortly be taken up for investigation at the technical laboratory, since a few samples of bleached shellac made here did not on examination reveal the presence of chlorine.

*Bleached Shellac: Its Preparation as a Local Industry.*—Mr. Fraymouth says "it is unlikely that white lac will ever be manufactured in India, because it remains hard only at low temperatures." India is the great shellac-producing country of the world, and it should really be her monopoly to manufacture white lac (bleached shellac) If chlorine is rendered available in large quantities and as a cheap commodity, then there is absolutely no reason why India should not be the seat of manufacture of bleached shellac. The most vital drawback to its local manufacture is the scarcity of chlorine, or, for the matter of that, cheap chlorine.

White shellac is at present unknown and unobtainable in the country, and owing to its rapid deterioration, unless made into polish, is not imported. Several of the Indian timbers cannot be properly finished without the use of bleached shellac, and a considerable addition to the uses of certain woods is sure to follow if the matter of polish can be handled locally.—*Journal of Indian Industries and Labour.*

## FUEL PROBLEMS OF THE FUTURE.*

By SIR GEORGE T. BEILBY, F.R.S.

(Concluded from p. 118).

WHEN coal is used for steam-raising under the best-known conditions, it is obvious that there is little to be gained in thermal efficiency by any preliminary sorting-out of the thermal units of the coal into fuels of higher availability. It is well-known that an efficiency of 75 to 80 per cent is attainable in steady practice. This is brought out by the results of the working during the first quarter of the present year at the two London power stations to which reference has already been made. At the station of the General Electric Supply Co., the average efficiency, less banking, was 75·5 per cent, though the average percentage of ash was 18·4. At the Durnford Road power house, the average efficiency was 78 per cent, and the average percentage of ash was 16. Supposing the coal used at these stations had been submitted to preliminary carbonisation and its thermal units sorted out into the forms of gas, tar, and coke, how would this have affected the evaporative efficiency of the total thermal units of the coal?

The coke would contain 70 per cent, the gas 12 per cent, the oils 11 per cent=93 per cent; intrinsic thermal loss 7 per cent, heat to be supplied for carbonisation 6 per cent=13 per cent; net thermal value of the products=80 per cent.

The high thermal availability of the rich gas would be thrown away if it were used for steam-raising; the fuel oil would be a boiler fuel decidedly superior to the original coal; and the coke would not be of more than equal value to the coal. Solely from the steam-raising point of view, therefore, a thermal loss would result, and not a gain, from the operation.

I at once admit that in special cases this thermal loss might be compensated for if a local market for the rich gas were available. In most cases, however, the margin of profit would be much too small to justify the extra capital expenditure required.

The valuable papers of Mr. D. Brownlie (*Engineering*, July 12 and 19, 1918; July 25 and Aug. 1, 1919; Dec. 10 and 17, 1920) throw a much-needed light upon the use of coal for steam-raising. His analysis of the statistics which he has collected shows that the amount of coal used for steam generation in this country for heat and power production is from 75 to 100 million tons per annum, or about one-half of the whole coal consumption. Mr. Brownlie's conclusions as to the comparative efficiency of the numerous boiler plants he has personally examined during the past seven or eight years, and the extension of these conclusions to cover the whole steam-raising practice of the United Kingdom, supply us with material on which some broad generalisations may be based. Mr. Brownlie divides the existing boiler installations in the United Kingdom into three classes—bad, average, and highly efficient Of the total number, 10 per cent are bad, 85 per cent are average, and 5 per cent are highly efficient. As regards the efficiencies of each class, with water-tube boilers, the bad give 61 per cent, the average give 69 per cent, and the highly efficient give 82 per cent; while with Lancashire boilers, the bad give 49 per cent, the average 60 per cent, and the highly efficient give 79 per cent.

If we take the minimum figure of 75 million tons as the amount of coal annually used for steam-raising, it is clear that the scope for economy is enormous; for even a moderate increase of efficiency of 10 per cent over all would result in a saving of 7½ million tons per annum. Mr. Brownlie's own experience of the savings to be effected by the reorganisation of existing plants leads him to take a much higher saving as a possibility. In the case of the colliery steam-boiler plants (the average efficiency of which he places at 51 per cent), he estimates that the coal bill for all the colliery plants in the country is 18½million tons, and that the efficffiiency might easily be raised by 10 to 15 per cent; while by the systematic use of colliery waste a further saving of saleable coal would be realised.

Mr. Brownlie's facts and figures are well worth the careful study of all who are seriously interested in fuel economy. These show the enor-

*Delivered in the theatre of the Institution of Civil Engineers, London. Inserted by favour of the *Gas Journal*, June 29, 1921.

mous possibilities in this direction which are actually within our grasp if we will only avail ourselves of the knowledge which already exists. No new and revolutionary discoveries are required for their realisation. The problem of the future which awaits solution is how to stimulate the practical interest of the owners of steam-raising plant throughout the country. It may be that the permanently increased cost of coal will supply the necessary stimulus· but this will only begin to take effect when the industry has settled down to more normal conditions. For steam-raising in this country, the cheapest form of fuel is coal or coke, if it is used under reasonably scientific conditions; and so long as this is the case, the use of fuels of higher availability will only be economically practicable under very special conditions.

In America the use of pulverised fuel is making steady progress, not only for metallurgical purposes (for some of which it is very suitable), but even for steam-raising. The case for steam-raising by this method is still, however, by no means clear.

The primary object of the coke industry is the production of hard coke for the manufacture of iron and steel. The coals must be of a special type. The therms obtained in the form of gas, though of high availability, are primarily used for the heating of the coke-ovens, for which therms of lower availability would do equally well. In a few instances in this country the surplus gas is sold to gas undertakings in the neighbourhood of the coke-ovens; and in these cases full advantage is taken of its high availability. In Northumberland and Durham the surplus gas from the coke-ovens is used for the generation of electricity by steam-boilers and engine; the current produced being fed into the main circuit of the Newcastle Power Co. In this case the high availability the gas therms is thrown away in doing work which could be done equally well by cheaper therms in the form of coal or coke. The tar and ammonia which are recovered from the coke-ovens take their place side by side with the same products of carbonisation in gasworks. The hard coke, owing to its density, and the practical absence of volatile matter, is quite unsuitable as a domestic fuel, except in specially constructed stoves or waterheaters.

The future development of the coking industry must mainly be determined by its intimate association with the iron and steel industry.

In the gas industry, the fuel problems of the future have a new interest since the publication of the report of the Fuel Research Board on the results of their inquiry into the subject of gas standards. As you are no doubt aware, the results of this inquiry led to the adoption by the Board of Trade of a new method of charging the consumer for the gas which passes through his meter. The volume of this gas is still measured and recorded; but the consumer no longer pays on thousands of cubic feet, but on the product of the multiplication of the number of cubic feet passed by the standard calorific value of the gas per cubic foot. The unit of charge is the "therm," which is the name adopted for 100,000 British thermal units. Under this system it is now possible to give gas undertakings a wide latitude in the selection of the standard of calorific value which they adopt, and therefore a much wider choice of the methods by which the gas is manufactured. In the report it was stated that the great gain for the gas undertakings under the new system would be that no undue legislative restrictions would limit them in their development of the most economical production of thermal units in the form of gas. It was pointed out that there was still great scope for this development, as, according to present practice, only from 21 to 24 per cent of the total potential thermal units of the coal is being sold in the form of gas.

To increase this percentage, two methods were available, both depending on the production of water gas by one or other of the reactions between steam and carbon at a high temperature. The first of these methods was the old-established one in which a portion of the coke produced in the retorts was transferred to a separate producer, in which it was raised to bright incandescence by an air-blast and then subjected to the action of a current of steam. The thermal efficiency of this operation ranged from 45 to 55 per cent, according to the method of blowing-up and steaming adopted. The second method has recently been chosen in connection with vertical retorts. In this case the water-gas reactions are carried out in the lower part of the column of red-hot coke in the retort itself, by passing through it a current of steam. The volume of gas produced is much increased, though its calorific value is reduced by the addition of water gas to the hydrocarbon gas resulting from the carbonisation of the coal.

It was foreseen by the Fuel Research Board that the introduction of the new thermal standard would open the way to a more general adoption of this method; and a setting of vertical retorts was installed at the Fuel Research Station with the object of obtaining trustworthy data as to the conditions and the limitations of the steaming process. A full report on the results of the experimental working during the past year was recently presented to the Institution of Gas Engineers.

As the experimental plant at the Fuel Research Station is especially adapted for the obtaining of full and accurate thermal and other data, it is now possible to speak with considerable confidence on the economic bearings of this process as applied to several distinct types of coal. Two of the questions which it was proposed to answer were:

1. Under pre-arranged conditions of temperature and percentage of steam, how will the yields of the principal products—gas, tar, coke, and ammonia—be affected in different types of coal?
2. To secure the increased yields of products, how much extra heat must be supplied to the retorts?

The gain which is of most importance to the gas industry is that of "therms" in the form of saleable gas. It had been common knowledge for some years that this gain by steaming was an assured one, if gas of a calorific value of 400 to 450 B.Th.U. could be established as a saleable commodity. It was not equally certain what the effect of steaming would be on the other products—tar, coke, and ammonia.

We can now say with confidence that there is not only a very substantial gain in therms in the form of gas, but also in the yields of tar and ammonia. I will only quote the results of one set of

tests, which were carried out on a South Yorkshire coal of good quality.

At a working temperature of 1260° C., and with 21 per cent of steam, the gains per ton of coal were: 22 therms in the form of gas; 34lb. of tar; and 6lb. of ammonium sulphate. While without steam only 23 per cent of the potential heat of the coal was obtained in the form of gas; with steam, 33 per cent was obtained. The extra heat which had to be supplied to the retorts in order to produce these results was ten therms per ton of coal carbonised. It is estimated that the additional value of the products obtained by steaming amount to at least 10s. per ton of coal carbonised.

The general adoption of steaming in vertical retorts will almost certainly be followed by a great extension of the use of this form of retort, and a very substantial saving will result, both as regards gas undertakings and consumers at large.

*Conclusions.*—From this brief review, it appears that coal is likely to remain for a long time the world's chief source of fuel. Its more efficient use may be secured :—

1. By more careful sorting and preparation at the mines.
2. By the improvement of boiler firing on well-known lines.
3. By the sorting-out of its combustible constituents into fuels of higher availability or convenience by preliminary carbonisation carried out either at high or low temperatures. This has an important bearing on the development of home sources of fuel oil and motor spirit and on the production of smokeless solid fuel for domestic purposes.

The development of oil shales as a source of liquid fuels is still only in its initial stages; but it has evidently a great future.

The problems of the utilisation of peat, which cover a wide range, both technically and economically, are mainly of local importance, and are not likely to affect the fuel supplies of the world to any great extent.

The production of alcohol on a really large scale as a motor fuel of high availability bristles with economic and technical difficulties; and it is still too soon to pronounce an opinion on the possibilities of the future.

Most, if not all, of these problems on their technical side are probably capable of solution by the skill and application of the industrial pioneers of the world; but the most difficult of the fuel problems of the future are those into which the human element enters so largely. At home, the relations of the wage-earning classes with the actual leaders who initiate and direct our industrial policy, and abroad, our relations with other nations who are equally interested with ourselves in the natural resources of the world, are profoundly affected by the spirit of the times. This spirit, as it is manifesting itself to-day, is fatal to the progress of reconstruction and development on any extensive scale; and we, whose chief interest in life lies in the control and use of the powers and resources of Nature for the service of man, can only continue to do the work next our hand while we cherish the hope that the better side of human nature, which we know is only temporarily overshadowed, will gradually reassert itself.

# CORRESPONDENCE.

## MINERS' CONFERENCE AND F.B.I.

*To the Editor of the Chemical News.*

SIR,—At the Miners' Conference at Llandudno on the 19th inst., Mr. Gavan Duffy was reported generally in the Press as having said that the Federation of British Industries had 376 of their members in the House of Commons; this group, in his opinion, possessing complete control over the Government.

Statements of this kind have been made by responsible Labour leaders in every part of the country, though without the slightest foundation. It seems necessary, therefore, to correct an error which such a large number of Labour publicists are making. The facts can be clearly stated as follows :—

The Federation of British Industries takes no part in politics whatever, and has never at any time supported or worked for Parliamentary candidates. It happens in the ordinary course of events that there are betwen 70 and 80 Members of Parliament who are connected with firms which are Members of the Federation, but in no single instance can it be said that the Federation had any part in these being elected.—I am, &c.,

J D. BENBOW HEBBERT
Director's Department.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences.* Vol. clxxiii., No. 6.

"New Spectrum of Cæsium."—By M. L. Dunoyer.

"New Revision of the Density of Gaseous Oxygen."—By MM. E. Moles and F. Gozalez.

"Synthesis and Dehydration of Ethyl-propyl-phenyl-cartinol."—By M. Vartkès Véramian.

# NOTES.

CONGRESS OF APPLIED CHEMISTRY.—The *Société de Chimie Industrielle de France* will hold a meeting of its many French and foreign members on October 9, 10, 11, and 12. This meeting, which will constitute a veritable congress of industrial chemistry, will comprise 34 sections, corresponding to the various applications chemistry: analytical chemistry; factory equipment; laboratory equipment; gas and coke industry; hydrocarbons, petrols; distillation of wood and derivatives; refrigeration industries; waters; metallurgy; electrometallurgy; precious metals; major chemical industries; electrochemistry; lime, cements, and building materials; glass and enamel manufacture and ceramics; minor chemical industries; rare earths and radio-active substances; colouring materials; pharmaceutical and photographic products; powders; explosives; essences and natural and synthetic perfumes; resins; lacs; varnishes, waxes; caoutchouc and substitutes; fats, soaps, candles, glycerines; cellulose paper; plastic materials and artificial textiles; bleaching, dyeing, printing; tinctorial extracts and tannins; tanning and allied in-

dustries; fermentation industries; oonology; cider manufacture; brewing; distilling; sugar manufacture; manufacture of starch and glucose; dairying; foods; agricultural chemistry; soils and the use of manures. Important questions will be discussed by the most renowned specialists. The Congress, which will be held at the Conservatoire des Arts et Metiers, will be opened on the evening of October 9 by a reception of the members The opening meeting will take place at 9.30 a.m. on the 10th. M. Dior, the Minister of Commerce, presiding. Many celebrities of the scientific and industrial world have promised to give lectures during the congress, and the closing meeting will take place on the 11th, at 5 o'clock, when M. Loncheur, Minister of the Liberated Districts, will take the chair. A general banquet will follow at the Palais d'Orsay, M. Lefebre du Prey, Minister of Agriculture presiding, and the next day the members of the Congress will pay visits to various factories.

EXHIBITION OF CHEMISTRY.—An Exhibition of Chemistry, organised under the patronage of the Minister of Commerce by the *Société de Chimie Industrielle* on the occasion of the First Annual Meeting will be held from October 7 to 16 at the Conservatoire Nationale des Arts et Métiers. This Exhibition, the germ of future chemical exhibitions, will include only two sections: the Equipment of the Laboratory and Industrial Control; and Colouring Materials. Most French firms are included amongst the exhibitors. The novelty and diversity of the goods and products which they propose to send cannot fail to attract many visitors interested in the progress and development of various branches of chemistry.

INSTITUTION OF ELECTRICAL ENGINEERS.—At a meeting of the Privy Council held at Buckingham Palace on Wednesday, August 10, 1921, the petition of the Institution for a Royal Charter of Incorporation was approved, and a Royal Charter has now been granted. His Majesty the King has also been graciously pleased to intimate his willingness to become Patron of the Institution.

TECHNICAL COLLEGE, BRADFORD.—The Calendar of the College for the Session 1921-22 gives details of the full-time (day) and part-time (mainly evening) courses in the departments of textile industries, chemistry, dyeing, mechanical, civil, and electrical engineering, and biology of the College. The full-time courses extend over three or four years, and lead to the Diploma of the College, and the part-time courses, which involve attendance on three evenings a week during three or five sessions, lead to Senior and Advanced Course Certificates of the College. The courses have been specially designed to meet the needs of students wishing to receive a technological training which will enable them to occupy higher positions in industry. The full-time courses in the College are of University standard, and candidates for admission to these courses who have not passed the Matriculation Examination or one of its equivalent examinations, are required to pass the College Entrance Examination, the standard of which is approximately the same as that of the Matriculation Examination. Special consideration is, however, given to the cases of students who have been in whole-time industrial employment for several years, and who may wish to enter one of the full-time courses. The full-time courses have recently been modified with a view to meeting the requirements of those candidates who present themselves for the Diploma of the College and who may wish, at the same time, to present themselves for one of the degree examinations of the University of London. The part-time (evening) courses in the College are intended to meet the needs of those students who are engaged in industry during the greater part of their time. These courses form a large and important part of the work of the College. Many of the advanced courses are attended by those students who have already completed systematic technological courses, and have entered industry, but who wish to keep abreast with the various developments which are continually taking place. In addition to the organised courses, the College also provides special facilities for those students who may wish to undertake advanced study. Students may also undertake research in the various departments of the College, and with a view to the further development of this part of the work of the College, additional equipment and accommodation is being provided. The advanced work of the College includes special post-graduate courses suitable for candidates wishing to prepare themselves for the examination for the Diploma in Public Health of the Royal College of Physicians and Surgeons. The equipment of the College is extensive, and includes a complete plant for the washing, carding, combing, spinning, weaving, dyeing, and finishing of textiles. A special feature of the equipment is the Power House, which has been arranged for demonstration purposes, and which supplies the whole of the power and light required by the College. Mention should also be made of the new engineering apparatus, which will provide special facilities for microphotographic work, for automobile engineering, and for heat treatment. Registration for the part-time courses in the College will take place from September 13 to 17, and for the full-time courses in the College from September 20 to 23. In view of the limited accommodation now available, applications for admission for the full-time courses should be made without delay.

JAPANESE LACQUER INDUSTRY.—The centres of the Japanese industry are Wajimi and Yamashiro in Tshikawa. Before the war business greatly declined because Chinese varnish was often employed, which is not so good, and the wood was not well prepared. Consequently the objects were not sufficiently resisting for dry climates of Europe and America. Moreover, German pasteboard imitations competed keenly with cheap Japanese lacquered articles. Consumption has now increased, but two-thirds of the varnish employed comes from China, where wild trees are tapped. The lacquer obtained is not sufficiently purified, and is inferior to the Japanese product. —*Matières Grasses*, July, 1921.

A PLATINUM SUBSTITUTE.—The employment of crucibles made with an alloy, *platino* (Au+Pt), is recommended by Mr. Van der Marck. These crucibles are not suitable for electrolytic estimates nor analyses made above 1000° C., but they are quite good for estimates of $CaCO_3$, $BaSO_4$, $Fe_2O_3$, ZnO, &c. The alloy in question is clearly inferior to platinum for sulphuric and nitric acids; it resists the action of KOH and $KNO_3$ at a red heat.—*Chimie et Industrie*, July, 1921.

Free British Propaganda at the Trieste Samples Fair.—The authorities of the Annual Trieste Samples Fair, which commences on Sept. 11, have invited H.M. Government to form a British Propaganda and Information Bureau at the Fair. The stand has been placed at the disposal of the British Consul-General free of charge, and the organisation of the Bureau has commenced. Trade catalogues, photographs, and general literature will be displayed on the stand, and information supplied in response to commercial enquires. At the same time, every effort will be made to stimulate the interests of the Italian, Balkan, and Levantine visitors to the Fair in British production generally, and in travel in the United Kingdom. The object of the Fair authorities in making their offer is to enable those British firms who cannot participate individually to make known the range of their products to the buyers at the Fair. There will be no expense to United Kingdom firms whose literature is displayed at the Propaganda Bureau, apart from the cost of forwarding it to Trieste. So far as possible all catalogues, &c., should be in Italian. Firms interested should despatch such matter by express post not later than September 1st to the British Consulate General, Trieste, marked "British Propaganda Bureau." As the space available is somewhat limited, the number of catalogues despatched by any one firm should not exceed 50, and of leaflets 500.

## NEW COMPANIES.

The under-mentioned particulars of New Companies recently registered are taken from the Daily Register compiled by Jordan & Sons, Limited, Company Registration Agents, Chancery Lane, W.C 2.

Byproducts Extractions, Limited.—(176337)—Registered August 17th, 1921. Donington House, Norfolk Street, Strand, W.C 2. To acquire an Invention in relation to the treatment, application or use for commercial utility or scientific purposes of Sewage and other Waste Nominal Capital: £10,000 in 10,000 Ordinary Shares of £1 each. Directors. H L. Davis, 7a, Courtfield Gardens, S.W.5.; W. Hunt, 23, Cecil Mansions, Balham, S.W.17; A. Lyle-Samuel, M P., Dower House, Sizewell-sum-Leiston, Suffolk, G. Sievwright, 25, Ryder Street, St. James's, S.W.; N. Sievwright, 25, Ryder Street, St. James's, S.W. Qualification of Directors: 1 Share. Remuneration of Directors. £100 each.

Rowand & Co., Limited.—(176354)—Registered August 17th, 1921. 1, Crosshall Street, Liverpool. To carry on the business of Chemists and Druggists, etc. Nominal Capital. £500 in 500 Shares of £1 each. Directors: E. M. Murphy, T. E Hughes. Qualification of Directors 1 Share. Remuneration of Directors: To be voted by Company.

D. T. Evans, Limited.—(176307)—Registered August 16th, 1921. To acquire and carry on the business of Wholesale and Retail Chemists and Druggists. Nominal Capital. £25,000 in 25,000 Shares of £1 each. Directors: D. T Evans, Farninghan Lodge, Margate (Governing Director); Dorothy C. Evans, Farninghan Lodge, Margate; E. Button. Qualification of Directors: 100 Shares. Remuneration of Directors: To be voted by Company.

## New Patents.

This List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W.C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

21170—Eisenwerkges.-Maximilianshutte.—Process for treatment of phosphorous compounds for manurial purposes. August 9.

21369—Gawalowski, A.—Process for production of synthetic camphor. August 11.

20969—Kulas, C.—Process for production of resinous products of condensation from phenol and formaldehyde. August 10.

21342—Stacey, F.—Dynamo-electric machines for producing oxides of nitrogen. August 11.

21321—Walker, D. D.—Fractional distallation of crude naphtha. August 11.

*Specifications published this Week.*

167219—Wade, H.—Process of catalytic oxidation.

149648—Schmiedel, T. and Klencke, H.—Process for the production of sulphuric acid.

167313—Spence & Sons, Ltd., P., Spence, H. and Craig, T. J. I.—Purification of sulphur.

143550—Nitrogen Corporation.—Production of ammonia.

157850—Haakh —Manufacture of oxyarylaldehydes.

*Abstract Published this Week.*

*Sodium Formate.*—Patent No. 165163.—Mr. M. Enderli, of Oestrich, Rheingau, Germany has Patented an improved process for producing Sodium Formate. Carbon Monoxide is introduced into water containing sodium sulphate and lime, the sodium sulphate being maintained at a concentration not greater than 7 per cent calculated as $Na_2SO_4$ This concentrated may be regulated by the presence of basic sodium calcium sulphate, $Na_4Ca_3(SO_4)_4(OH)_2$, obtained by heating calcium or sodium hydroxide in water with sodium sulphate and calcium sulphate, or with substances containing or forming these compounds, *e.g.*, calcium sodium sulphate or sodium chloride and calcium sulphate. Another method of maintaining the sodium sulphate concentration consists in adding sodium sulphate or calcium sodium sulphate or basic sodium calcium sulphate to replace the sulphate as it is consumed, excess of lime being either present in the reaction vessel or gradually added thereto.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

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# BRITISH ASSOCIATION
## FOR THE
## ADVANCEMENT OF SCIENCE.

EDINBURGH, 1921.

INAUGURAL ADDRESS OF THE PRESIDENT.

SIR T. EDWARD THORPE, C.B., D.Sc., Sc D., LLD , F.R.S., Hon. F.R.S. Edin.

THE British Association for the Advancement of Science owes its origin, and, in great measure, its specific aims and functions, to the public spirit and zeal for the interests of science of Scotsmen. Its virtual founder was Sir David Brewster; its scope and character were defined by Principal Forbes In constitution it differed from the migratory scientific associations existing on the Continent, which mainly served to promote the social intercourse of their members by annual gatherings, in that it was to be a permanent organisation, with a settled establishment and headquarters, which should have not merely its yearly reunions, but which, "by methods and by influence peculiarly its own, should ontinue to operate during the intervals of these public assemblies, and should aspire to give an impulse to every part of the scientific system; to mature scientific enterprise; and to direct the labours requisite for discover."

Although, for reasons of policy, it was decided that its first meeting of September 27, 1831, should be held at York, as the most central city for the the three kingdoms, and its second and third meetings at the ancient Universities of Oxford and Cambridge respectively, it was inevitable that the Association should seize the earliest opportunity to visit the Metropolis of Scotland where, as an historical fact, it may be said to have had its origin.

The meeting in this city of September 8, 1834, was noteworthy for many reasons. It afforded the first direct proof that the Association was fulfilling its purpose. This was shown by the popular appreciation which attended its activities, by the range and character of its reports on the state and progress of science, by the interest and value of its sectional proceeding, and by the mode in which its funds were employed. In felicitous terms the president of the preceding year, the Rev. Professor Sedgwick, congratulated the gathering "on the increased strength in which they had assembled, in a place endeared to the feelings of every lover of science by so many delightful and elevating recollections, especially by the recollection of the great men whom it had fostered, or to whom it had given birth." In a few brief sentences Professor Sedgwick indicated the great power which this Association is able to apply towards the advancement of science by combination and united action, and he supported his argument by pointing to the results which it had already achieved during the three short years of its existence. Professor Sedgwick's words are no less true to-day. His contention that one of the most important funcions of this philosophical union is to further what he termed the "commerce of ideas" by joint discussions on subjects of kindred interest, has been endorsed by the recent action of the Council in bringing the various sections into still closer touch with each other with a view to the discussion of common problems of general interest. This slight reorganisation of the work of the Sections, which is in entire accord with the spirit and aims of the Association, as defined by its progenitors and formulated in its constitution, will take effect during the present meeting. Strictly speaking, such joint sectional discussions are not unknown in our history, and their utility and influence have been freely recognised. But hitherto the occasions have been more or less informal. They are now, it is hoped, to be part of the regular official procedure of the meetings, to which it is anticipated they will afford additional interest and value.

Another noteworthy change in our procedure is the introduction of discussions on the addresses of the Presidents of Sections. Hitherto these addresses have been formally read and never discussed. To the extent that they have been brief chronicles of the progress of the special departments of science with which the section is concerned they have given but little opportunity for discussion. With the greatly increased facilities which now exist for every worker to keep himself informed of the development of the branch of knowledge in which he is more particularly interested, such *résumés* have in great measure lost their true purpose, and there has, consequently, been a growing tendency of late years for such presidential addresses to deal with contemporary topics of general interest and of fundamental importance, affording ample opportunity for a free exchange of opinion. The experiment will certainly conduce to the interest of the proceedings of the sections, and will contribute to the permanent value of their work. We see in these several changes the development of ideas connected with the working of the Association which may be said to have had their birth at its first meeting in Edinburgh, eighty-seven years ago.

Sixteen years later, that is, on July 21, 1850, Edinburgh again extended her hospitality to the British Association, which then honoured itself by electing the learned Principal of the United Colleges of St. Salvator and St. Leonard, St. Andrews, to the presidential chair—at once a tribute to Sir David Brewster's eminence as a natural philosopher, and a grateful recognition of his services to this body in suggesting and promoting its formation.

On the occasion of his inaugural address, after a brief account of recent progress in science, made with the lucidity of expresson which characterised all the literary efforts of the learned biographer of Newton and versatile editor of the *Edinburgh Encyclopædia*, the *Edinburgh Magazine*, and the *Edinburgh Journal of Science*, the President dwelt upon the beneficient influence of the Association in securing a more general attention to the objects of science, in effecting a removal of disadvantages of a public kind that impeded its progress. It was largely to the action of the Asso-

ciation, assisted by the writings and personal exertions of its members, that the Government was induced to extend a direct national encouragement to science and to aid in its organization

Brewster had a lofty ideal of the place of science in the intellectual life of a community, and of the just position of the man of science in the social scale. In well-weighed words, the outcome of matured experience and of an intimate knowledge of the working of European institutions created for the advancement of science and the diffusion of knowledge, he pleaded for the establishment of a national institution in Britain, possessing a class of resident members who should devote themselves wholly to science—with a place and station in society the most respectable and independent—"free alike," as Playfair put it, "from the embarrassments of poverty or the temptations of wealth." Such men, "ordained by the State to the undivided functions of science," would, he contended, do more and better work than those who snatch an hour or two from their daily toil or nightly rest.

This ideal of "combining what is insulated, and uniting in one great institution the living talent which is in active but undirected and unbefriended exercise around us," was not attained during Brewster's time; nor, notwithstanding the reiteration of incontrovertible argument during the past seventy years, has it been reached in our own.

I have been led to dwell on Sir David Brewster's association with this question of the relations of the State towards research for several reasons. Although he was not the first to raise it—for Davy more than a century ago made it the theme of presidential addresses, and brought his social influence to bear in the attempt to enlist the practical sympathy of the Government—no one more consistently urged its national importance, or supported his case with a more powerful advocacy, than the Principal of the University of Edinburgh. It is only seemly, therefore, that on this particular occasion, and in this city of his adoption, where he spent so much of his intellectual energy, I should specially allude to it. Moreover, we can never forget what this Association owes to his large and fruitful mind. Every man is a debtor to his profession, from which he gains countenance and profit. That Brewster was an ornament to his is acknowledged by every lover of learning. That he endeavoured to be a help to it was gratefully recognised during his lifetime. After his death it was said of him that the improved position of men of science in our time is chiefly due to his exertions and his example.

I am naturally led to connect the meeting of 1850 with a still more memorable gathering of this Association in this city. In August, 1871—just over half-a-century ago—the British Association again assembled in Edinburgh under the presidency of Lord Kelvin—then Sir William Thomson It was an historic occasion by reason of the address which inaugaurated its proceedings. Lord Kelvin, with characteristic force and insistence, still further elaborated the theme which had been so signal a feature of Sir David Brewster's address twenty years previously: "Whether we look to the honour of England," he said, "as a nation which ought always to be the foremost in promoting physical science, or to those vast economical advantages which must accrue from such establishments, we cannot but feel that experimental research ought to be made with us an object of national concern, and not left, as hitherto, exclusively to the private enterprise of self-sacrificing amateurs, and the necessarily inconsecutive action of our present Governmental Departments and of casual committees."

Lord Kelvin, as might have been anticipated, pleaded more especially for the institution of physical observatories and laboratories for experimental research, to be conducted by qualified persons, whose duties should be not teaching, but experimenting. Such institutions as then existed, he pointed out, only afforded a very partial and inadequate solution of a national need. They were, for the most part, "absolutely destitute of means, material, or *personnel*, for advancing science, except at the expense of volunteers, or of securing that volunteers should be found to continue such little work as could then be carried on."

There were, however, even then, signs that the bread cast upon the waters was slowly returning after many days. The establishment of the Cavendish Laboratory at Cambridge, by the munificence of its then Chancellor, was a notable achievement. Whilst in its constitution as part of a university discipline it did not wholly realize the ideal of the two Presidents, under its successive directors, Prof. Clerk-Maxwell, the late Lord Rayleigh, and Sir J. J. Thomson, it has exerted a profound influence upon the development of experimental physics, and has inspired the foundation of many similar educational institutions in this country. Experimental physics has thus received an enormous impetus during the last fifty years, and although in matters of science there is but little folding of the hands to sleep, "the divine discontent" of its followers has little cause for disquietude as regards the position of physics in this country.

In the establishment of the National Physical Laboratory we have an approach to the ideal which my predecessors had so earnestly advocated Other Presidents, among whom I would specially name the late Sir Douglas Galton, have contributed to this consummation. The result is a remarkable testimony to the value of organised and continuous effort on the part of the British Association in forming public opinion and in influencing Departmental action. It would, however, be ungrateful not to recall the action of the late Lord Salisbury—himself a follower of science and in full sympathy with its objects—in taking the first practical steps towards the creation of this magnificent national institution. I may be allowed, perhaps, to refer to this matter, as I have personal knowledge of the circumstances, being one of the few survivors of the Committee which Lord Salisbury caused to be formed, under the chairmanship of the late Lord Rayleigh, to enquire and report upon the expediency of establishing an institution in Great Britain upon the model of certain State-aided institutions already existing on the Continent, for the determination of physical constants of importance in the arts, for investigations in physical problems bearing upon industry, for the standardisation and verification of physical instruments, and for the general

purposes of metrology. I do not profess to give the exact terms of the reference to the Committee, but, in substance, these were recognised to be the general aims of the contemplated institute. The evidence we received from many men of science, from Departmental officers, and from representatives of engineering and other industrial establishments was absolutely unanimous as to the great public utility of the projected laboratory. It need hardly be said that the opportunity called forth all the energy and power of advocacy of Lord Kelvin, and I well remember with what strength of conviction he impressed his views upon the Committee. That the National Physical Laboratory has, under the ability, organising power, and business capacity of its first director, Sir Richard Glazebrook, abundantly justified its creation is recognised on all hands. Its services during the four years of war alone are sufficient proof of its national value. It has grown to be a large and rapidly increasing establishment, occupying itself with an extraordinary range of subjects, with a numerous and well-qualified staff, engaged in determinative and research work on practically every branch of pure and applied physics. The range of its activities has been further increased by the establishment since the war of co-ordinating research boards for physics, chemistry, engineering, and radio-research. Government Departments have learned to appreciate its services. The photometry division, for example, has been busy on experiments on navigation lamps for the Board of Trade, on miners' lamps for the Home Office, and on motorcar headlamps for the Ministry of Transport, and on the lighting of the National Gallery and the Houses of Parliament. Important work has been done on the forms of ships, on the steering and manœvring of ships, on the effect of waves on ship resistance, on the interaction between passing ships, on seaplane floats, and on the hulls of flying-boats.

It is also actively engaged in the study of problems connected with aviation, and has a well ordered department for aerodynamical research.

It can already point to a long and valuable series of published researches, which are acknowledged to be among the most important contributions to pure and applied physics which this country has made during recent years.

I may be pardoned, I hope, for another personal reference, if I recall that it was at the Edinburgh meeting, under Lord Kelvin's presidency, fifty years ago, that I first became a member of this Assocition, and had the honour of serving it as one of the secretaries of its chemical section. Fifty years is a considerable span in the life of an individual, but it is a relatively short period in the history of science. Neverless, those fifty years are richer in scientific achievement and in the importance and magnitude of the utilitarian applications of practically every branch of science than any preceding similar interval. The most cursory comparison of the state of science, as revealed in his comprehensive address, with the present condition of those departments on which he chiefly dwelt, will suffice to show that the development has been such that even Lord Kelvin's penetrative genius, vivid imagination, and sanguine temperament could hardly have anticipated. No previous half-century in the history of science has witnessed such momentous and far-reaching achievements. In pure chemistry it has seen the discovery of argon by Rayleigh of radium by Madame Curie, of helium as a terrestrial element by Ramsay, of neon, xenon, and krypton by Ramsay and Travers, the production of helium from radium by Ramsay and Soddy, and the isolation of fluorine by Moissan. These are undoubtedly great discoveries, but their value is enormously enhanced by the theoretical and practical consequences which flow from them.

In applied chemistry it has witnessed the general application of the Gilchrist-Thomas process of iron-purification, the production of calcium cyanamide by the process of Frank and Caro, Sabatier's process of hydrogenation, a widespread application of liquefied gases, and Haber's work on ammonia synthesis—all manufacturing processes which have practically revolutionized the industries with which they are concerned.

In pure physics it has seen the rise of the electron theory, by Lorentz; Hertz's discovery of electro-magnetic waves; the investigation of cathode rays by Lenard, and the elucidation of crystal structure by Bragg.

It has seen, moreover, the invention of the telephone, the establishment of incandescent lighting, the electric transmission of force, the invention of the cinematograph, of wireless telegraphy, the aplication of the Röntgen rays, and the photographic reproduction of colour.

In physical chemistry, it has witnessed the creation of stereo-chemistry by Van t'Hoff and Le Bel, Gibbs' work on the phase rule, Van t'Hoff's theory of solutions, Arrhenius's theory of ionic dissociation, and Nernst's theory of the galvanic cell.

Such a list is far from complete, and might be greatly extended. But it will at least serve to indicate the measure of progress which the world owes to the development and application during the last fifty years of the two sciences—physics and chemistry—to which Lord Kelvin specially referred.

The more rapid dissemination of information concerning the results of recent or contemporary investigation, which Lord Kelvin so strongly urged as 'an object to which the powerful action of the British Association would be thoroughly appropriate,' has been happily accomplished. The timely aid of the Association in contributing to the initial expense of preparing and publishing monthly abstracts of foreign chemical literature by the Chemical Society is gratefully remembered by British chemists. The example has been followed by the greater number of our scientific and technical societies, and the results of contemporary inquiry in every important branch of pure and applied science are now quickly brought to the knowledge of all interested workers. In fact, as regards the particular branch of science with which I am more directly concerned, the arrangements for the preparation and dissemination of abstracts of contemporary foreign chemical literature are proving to be a veritable embarrassment of riches, and there is much need for co-operation among the various distributing societies. This need is especially urgent at the present time owing to the greatly increased cost of paper, printing, binding, and indeed of every item connected with publication, which expense, of course,

ultimately falls upon the various societies and their members. The problem, which has already received some attention from those entrusted with the management of the societies referred to, is not without its difficulties,but these are not insoluble. There is little doubt that a resolute and unanimous effort to find a solution would meet with success.

The present high cost of book production, which in the case of specialised books is about three times what it was in 1914, is exercising a most prejudicial effect upon the spread of scientific knowledge. Books on science are not generally among the 'best sellers.' They appeal to a comparatively limited and not particularly wealthy public, largely composed of the professional classes who have suffered in no small measure from the economic effects of the war. The present high price of this class of literature is to the public detriment. Eventually it is no less to the detriment of the printing and publishing trades. Publishers are well aware of this fact, and attempts are being made by discussions between employers and the executives of the Typographical Association and other societies of compositors to reach an equitable solution, and it is greatly to be hoped that it will be speedily found.

All thinking men are agreed that science is at the basis of national progress. Science can only develop by research. Research is the mother of discovery,and discovery of invention. The industrial position of a nation, its manufactures and commerce, and ultimately its wealth, depend upon invention. Its welfare and stability largely rest upon the equitable distribution of its wealth. All this seems so obvious, and has been so frequently and so convincingly stated, that it is superfluous to dwell upon it in a scientific gathering to-day.

A late distnguished Admiral, you may remember, insisted on the value of reiteration. On this particular question it was never more needed than now. The crisis through which we have recently passed requires it in the interest of national welfare. Of all post-war problems to engage our serious attention, none is more important in regard to our position and continued existence than the nation's attitude towards science and scientific research, and there is no more opportune time than the present in which to seek to enforce the teaching of one of the most pregnant lessons of our late experience.

It is, unfortunately, only too true that the industrial world as in the past underrated the value of research. One indication that the nation is at length aroused to its importance is to be seen in the establishment of the Department of Scientific and Industrial Research, with its many subordinate associations. The outbreak of the Great War, and much in its subsequent history, revealed, as we all know, many national shortcomings, due to our indifference to and actual neglect of many things which are at the root of our prosperity and security During the War, and at its close various attempts, more or less unconnected, were made to find a remedy. Of the several committees and boards which were set up, those which still exist have now been co-ordinated, and brought under the control of a central organization—the Department of Scientific and Industrial Research. Research has now become a national and State-aided object. For the first time in our history its pursuit with us has been organized by Government action. As thus organized, it seeks to fulfil the aspirations to which I have referred, whilst meeting many of the objections which have been urged against the endowment of research. It must be recognised that modern ideas of democracy are adverse to the creation of places to which definite work is not assigned and from which definte results do not emanate This objection, which strikes at the root of the establishment of such an institution as Sir David Brewster contemplated, is, to a large extent, obviated by the scheme of the Department of Scientific and Industrial Research. It does not prescribe or fetter research, but, whilst aiding by personal payments the individual worker, leaves him free to pursue his enquiry as he thinks best. Grants are made, on the recommendation of an Advisory Council of experts, to research workers in educational institutions and elsewhere in order to promote research of high character on fundamental problems of pure science or in suitable cases on problems of applied science. Of the boards and committees and similar organizations established prior to or during the War, or subsequent to it, with one or two exceptions, all are now directly under the Department. They deal with a wide range of subjects, such as the Building Research Board, established early in 1920 to organize and supervise investigations on building materials and construction, to study structural failures, and to fix standards for structural materials. The Food Investigation Board deals with the preservation by cold of food, and with the engineering problems of cold storage, with the chemistry of putrefaction, and the agents which induce it, with the bionomics of moulds, and the chemistry of edible oils and fats. The Fuel Research Board is concerned with the immediate importance of fuel economy and with investigations of the questions of oil-fuel for the Navy and Mercantile Marine, the survey of the national coal resources, domestic heating, air polution, pulverised fuel, utilization of peat, the search for possible substitutes for natural fuel oil, and for practicable sources of power alcohol.

The Geological Survey Board has taken over the Geological Survey of Great Britain and the control of the Museum of Practical Geology. The Maintenance of the National Physical Laboratory, originally controlled by a General Board and an Executive Committee appointed by the President and Council of the Royal Society, is now transferred to the Department of Scientific and Industrial Research. A Mines Research Committee and a Mine Rescue Apparatus Committee are attached to the Department. The former is concerned with such questions as the determination of the geothermic gradient, the influence of temperature of intake and return air on strata, the effect of seasonal changes on strata temperature of intakes, the cooling effect due to the evolution of fire-damp, heat production from the oxidation of timber, etc. The Department is also directing enquiries on the preservation and restoration of antique objects deposited in the British Museum. It is concerned with the gauging of rivers and tidal currents, with special reference to a hydrographical survey of Great Britain in relation to the national resources of

water-power. In accordance with the Government policy, four co-ordinating boards have been established to organize scientific work in connection with the fighting forces, so as to avoid unnecessary overlapping and to provide a single direction and financial control. The four boards deal, respectively, with chemical and physical problems, problems of radio-research, and engineering. These boards have attached to them various committees dealing with special enquiries, some of which will be carried out at the National Physical Laboratory. The Government have also authorized the establishment of a Forest Products Research Board.

The Department is further empowered to assist learned or scientific societies and institutions in carrying out investigations. Some of these were initiated prior to the War, and were likely to be abandoned owing to lack of funds. Whenever the investigation has a direct bearing upon a particular industry that had not hitherto been able to establish a Research Association, it had been a condition of a grant that the institution directing the research should obtain contributions towards the cost on a £ for £ basis, either directly through its corporate funds or by special subscriptions from interested firms. On the formation of the appropriate association the research is, under suitable safeguards, transferred to it for continuance. The formation of a number of Research Associations has been stimulated, dealing, for example, with scientific instruments, non-ferrous metals, glass, silk, refractories, electrical and allied industries, pottery, etc.

Grants are made to Research Associations formed voluntarily by manufacturers for the purposes of research, from a fund of a million sterling, placed at the disposal of the Research Department for this purpose. Such Associations, to be eligible for the grant, must submit Articles of Association for the approval of the Department and the Board of Trade. If these are approved, licences are issued by the Board of Trade recognizing the Associations as limited liability companies working without profits. Subscriptions paid to an Association by contributing firms are recognized by the Board of Inland Revenue as business costs of the firms, and are not subject to income or excess profits taxes. The income of the Association is similarly free of income tax. Grants are ordinarily made to these Associations on the basis of £1 for every £1 raised by the Association between limits depending upon the particular industry concerned. In the case of two Research Associations grants are made at a higher rate than £ for £, as these industries are regarded as having a special claim to State assistance on account of their 'pivotal character. The results of research are the sole property of the Association makng them, subject to certain rights of veto possessed by the Department for the purposes of ensuring that they are not communicated to foreign countries, except with the consent of the Department, and that they may be made available to other interested industries and to the Government itself on suitable terms.

These arrangements have been found to be generally satisfactory, and at the present time twenty-four of such Research Associations have been formed to whom licences have been issued by the Board of Trade. Others are in process of formation, and may be expected to be at work at an early date. These Research Associations are concerned with nearly all our leading industries. The official addresses of most of them are in London; others have their headquarters in Manchester, Leeds, Sheffield, Northampton, Coventry, Glasgow, and Belfast.

The Department has further established a Records Bureau, which is responsible for receiving, abstracting, filing and collating communications from research workers, boards, institutions, or associations related to or supervised by the Department. This information is regarded as confidential, and will not be communicated except in writing, and after consultation with the research worker or organization from which it has been received. Also such non-confidential information as comes into the possession of the Department which is of evident or probable value to those working in touch with the Department is collected and filed in the Bureau and made generally available.

It is also a function of the Bureau to effect ecomomy in preventing repetition and overlapping of investigations and in ensuring that the fullest possible use is made of the results of research. Thus, the programmes of Research Associations are compared in order to ensure that researches are not unwittingly duplicated by different Research Associations. Sometimes two or more Research Associations may be interested in one problem from different points of view, and when this occurs it may be possible for the Bureau to arrange a concerted attack upon the common problem, each Research Association undertaking that phase of the work in which it is specially interested and sharing in the general results.

As researches carried out under the Department frequently produce results for which it is possible to take out patents, careful consideration has been given to the problems of policy arising on this subject, and other Government Departments also interested have been freely consulted. As the result, an Inter-Departmental Committee has been established with the following terms of reference:

(1) To consider the methods of dealing with inventions made by workers aided or maintained from public funds, whether such workers be engaged (*a*) as research workers, or (*b*) in some other technical capacity, so as to give a fair reward to the inventor and thus encourage further effort, to secure the utilization in industry of suitable inventions and to protect the national interest, and

(2) To outline a course of procedure in respect of inventions arising out of State-aided or supported work which shall further these aims and be suitable for adoption by all Government Departments concerned.

About forty patents have been taken out by the Department jointly with the inventors and other interested bodies, but of these, nine have subsequently been abandoned. At least five patents have been developed to such a stage as to be ready for immediate industrial application.

It will be obvious from this short summary of the activities of the Department, based upon information kindly supplied to me by Sir Francis Ogilvie, that this great scheme of State-aided research has been conceived and is administered

on broad and liberal lines. A considerable number of valuable reports from its various boards and committees have already been published, and others are in the press, but it is, of course, much too soon to appreciate the full effects of their operations. But it can hardly be doubted that they are bound to exercise a profound influence upon industries which ultimately depend upon discovery and invention. The establishment of the Department marks an epoch in our history. No such comprehensive organization for the application of science to national needs has ever been created by any other State. We may say we owe it directly to the Great War. Even from the evil of that great catastrope there is some soul of goodness would we observingly distil it out.

I turn now to a question of scientific interest which is attracting general attention at the present time. It is directly connected with Lord Kelvin's address fifty years ago.

The molecular theory of matter—a theory which in its crudest form has descended to us from the earliest times and which has been elaborated by various speculative thinkers through the intervening ages, hardly rested upon an experimental basis until within the memory of men still living. When Lord Kelvin spoke in 1871, the best-established development of the molecular hypothesis was exhibited in the kinetic theory of gases as worked out by Joule, Clausius, and Clerk-Maxwell. As he then said, no such comprehensive molecular theory had ever been imagined before the nineteenth century. But, with the eye of faith, he clearly perceived that, definite and complete in its area as it was, it was 'but a well-drawn part of a great chart, in which all physical science will be represented with every property of matter shown in dynamical relation to the whole. The prospect we now have of an early completion of this chart is based on the assumption of atoms. But there can be no permanent satisfaction to the mind in explaining heat, light, elasticity, diffusion, electricity, and magnetism, in gases, liquids and solids, and describing precisely the relations of these different states of matter to one another by statistics of great numbers of atoms when the properties of the atom itself are simply assumed. When the theory, of which we have the first instalment in Clausius and Maxwell's work, is complete, we are but brought face to face with a superlatively grand question: What is the inner mechanism of the atom?'

If the properties and affections of matter are dependent upon the inner mechanism of the atom, an atomic theory, to be valid, must comprehend and explain them all. There cannot be one kind of atom for the physicist and another for the chemist. The nature of chemical affinity and of valency, the modes of their action, the difference in characteristics of the chemical elements, even their number, internal constitution, periodic position, and possible isotopic rearrangements must be accounted for and explained by it. Fifty years ago, chemists, for the most part, rested in the comfortable belief of the existence of atoms in the restricted sense in which Dalton, as a legacy from Newton, had imagined them. Lord Kelvin, unlike the chemists, had never been in the habit of 'evading questions as to the hardness or indivisibility of atoms by virtually assuming them to be infinitely small and infinitely numerous' Nor, on the other hand, did he realize, with Boscovich, the atom 'as a mystic point endowed with inertia and the attribute of attracting or repelling other such centres.' Science advances not so much by fundamental alterations in its beliefs as by additions to them. Dalton would equally have regarded he atom 'as a piece of matter of measureable dimensions, with shape, motion, and laws of action, intelligible subjects of scientific investigation.'

In spite of the fact that the atomic theory, as formulated by Dalton, has been generally accepted for nearly a century, it is only within the last few years that physicists have arrived at a concepion of the structure of the atom sufficiently precise to be of service to chemists in connection with the relation between the properties of elements of different kinds, and in throwing light on the mechanism of chemical combination.

This further investigation of the 'superlatively grand question—the inner mechanism of the atom'—has profoundly modified the basic conceptions of chemistry. It has led to a great extension of our views concerning the real nature of the chemical elements. The discovery of the electron, the production of helium in the radioactive disintegration of atoms, the recognition of the existence of isotopes, the possibility that all elementary atoms are composed either of helium atoms or of atoms of hydrogen and helium, and that these atoms, in their turn, are built up of two constituents, one of which is the electron, a particle of negative electricity whose mass is only 1/1800 of that of an atom of hydrogen, and the other a particle of positive electricity whose mass is practically identical with that of the same atom—the outcome in short, of the collective work of Soddy, Rutherford, J. J. Thomson, Collie, Moseley and others—are pregnant facts which have completely altered the fundamental aspects of the science. Chemical philosophy has, in fact, now definitely entered on a new phrase.

Looking back over the past, some indications of the coming change might have been perceived wholly unconnected, of course, with the recent experimental work which has served to ratify it. In a short paper entitled "Speculative Ideas respecting the Constitution of Matter," originally published in 1863,, Graham conceived that the various kinds of matter, now recognised as different elementary substances, may possess one and the same ultimate or atomic molecule existing in different conditions of the movement. This idea, in its essence, may be said to be as old as the time of Leucippus. To Graham as to Leucippus "the action of the atom as one substance taking various forms by combinations unlimited, was enough to account for all the phenomena of the world. By separtion and union with constant motion all things could be done." But Graham developed the conception by independent thought, and in the light of experimentally ascertained knowledge which the world owes to his labours. He might have been cognisant of the speculations of the Greeks, but that is no evidence that he was knowingly influenced by them. In his paper Graham uses the terms atom and molecule if not exactly in the same sense that modern teaching demands, yet very different from that hitherto required by the limitations of contemporary chemical doctrine. He conceives of a lower order of atoms than the chemical atom of Dalton, and

founds on his conception an explantion of chemical combination based upon a fixed combining measure, which he terms *metron* its relative weight being one of hydrogen, sixteen for oxygen, and so on with the so-called "elements." Graham, in fact, like Davy before him, never committed himself to a belief in the indivisibility of the Daltonian atom. The origin-original atom may, he thought, be far down.

The idea of a primordial ylé, or of the essential unity of matter, has persisted throughout the ages, and, in spite of much experimental work some of it of the highest order, which was thought to have demolished it, it has survived, revivified and supported by analogies and arguments drawn from every field of natural inquiry. This idea of course was at the basis of the hypothesis of Prout, but which, even as modified by Dumas, was held to be refuted by the momumental work of Stas. But, as pointed out by Marignac and Dumas, anyone who will impartially look at these facts can hardly escape the feeling that there must be some reason for the frequnt recurrence of atomic weights differing by so little from the numbers required by the law which the work of Stas was supposed to disprove. The more exact study within recent years of the methods of determining atomic weights, the great improvement in experimental appliances and technique, combined with a more rigorous standard of accuracy demanded by a general recognition of the far-reaching importance of an exact knowledge of these physical constants, has resulted in intensifying the belief that some natural law must at the basis of the fact that so many of the most carefully determined atomic weights on the oxygen standard are whole numbers. Nevertheless there were well authenticated exceptions which seemed to invalidate its universality. The proved fact that a so-called element may be a mixture of isotopes—substances of the same chemical attributes but of varying atomic weight—has thrown new light on the question. It is now recognised that the fractional values independently established in the case of any one element by the most accurate experimental work of the various investigators are, in effect, "statistical quantities" dependent upon a mixture of isotopes. This result, indeed, is a necessary corollary of modern conceptions of the inner mechanism of the atom. The theory that all elementary atoms are composed of helium atoms, or of helium and hydrogen atoms, may be regarded as an extension of Prout's hypothesis, with, however, this important distinction, that whereas Prout's hypothesis was at best a surmise, with little, and that little only weak, experimental evidence to support it, the new theory is directly deduced from well-established facts. The hydrogen isotope $H_3$, first detected by J. J. Thomson, of which the existence has been comfirmed by Aston, would seem to be an integral part of atomic structure. Rutherford, by the disruption of oxygen and nitrogen has also isolated a substance of mass 3 which enters into the structure of atomic nuclei, but the which he regards as an isotope of helium, which itself is built up of four hydrogen nuclei together with two cementing electrons. The atomic nuclei of elements of even atomic number would appear to be composed of helium nuclei only, or of helium nuclei with cementing electrons; whereas those of elements of odd atomic number are made up of helium and hydrogen nucl together with cementing electrons. In the cas of the lighter elements of the latter class th number of hydrogen nuclei associated with th helium nuclei is invariably three, except in tha of nitrogen where it is two. The frequent occur rence of this group of three hydrogen nucle indicates that it is structurally an istope of hydro gen with an atomic weight of three and a nuclea charge of one. It is surmised that it is identica with the hypothetical 'nebulium' from which ou 'elements' are held by astro-physicists to be origin ally produced in the stars through hydrogen an helium.

These results are of extraordinary interest a bearing on the question of the essential unity o matter and the mode of genesis of the elements Members of the British Association may recal the suggestive address on this subject of the lat Sir William Crookes, delivered to the Chemica Section at the Birmingham meeting of 1886, i which he questioned whether there is absolut uniformity in the mas- of the atoms of a chemica element, as postulated by Dalton. He thought with Marignac and Schutzenberger, who had pre viously raised the same doubt, that it was no improbable that what we term an atomic weigh merely represents a mean value around which th actual weights of the atoms vary within narrow limits, or, in other words, that the mean mass i "a statistical constant of great stability". N valid experimental evidence in support of thi surmise was or could be offered at the time it wa uttered. Maxwell pointed out that the phenomen of gaseous diffusion, as then ascertained, woul seem to negative the supposition. If hydrogen for example, were composed of atoms of varyin mass, it should be possible to separate the lighte from the heavier atoms by diffusion through porous septum. 'As no chemist' said Maxwell 'has yet obtained specimens of hydrogen differin in this way from other specimens, we conclude tha all the molecules of hydrogen are of sensibly th same mass, and not merely that their mean mas is a statistical constant of great stability.' (Clerk Maxwell, Art. 'Atom' *Ency. Brit.* 9th Ed.) Bu against this it may be doubted whether an chemist had ever made experiments sufficientl precise to solve this point.

The work of Sir Norman Lockyer on the spec troscopic evidence for the dissociation of 'ele mentary' matter at transcendental temperatures and the possible synthetic intro-stellar productio of elements, through the helium of which he orig inally detected the existence, will also find its du place in the history of this new philosophy.

Sir J. J. Thomson was the first to afford direc evidence that the atoms of an element, if no exactly of the same mass, were at least approxi mately so, by his method of analysis of positiv rays. By an extension of this method Mr. F. W Aston has succeeded in showing that a number o elements are in reality mixtures of isotopes. I has been proved, for example, that neon, whic has a mean atomic weight of about 20.2, consis of two isotopes having the atomic weights re pectively of 20 and 22, mixed in the proportio of 90 per cent of the former with 10 per cent o the latter. By fractional diffusion through porous septum an apparent difference of densit of 0.7 per cent between the lightest and heavie fractions was obtained. The kind of experime

which Maxwell imagined proved the invariability of the hydrogen atom has sufficed to show the converse in the case of neon.

The element chlorine has had its atomic weight repeatedly determined, and, for special reasons, with the highest attainable accuracy. On the oxygen standard it is 35.46, and this value is accurate to the second decimal place. All attempts to prove that it is a whole number—35 or 36—have failed. When, however, the gas is analysed by the same method as that used in the case of neon it is found to consist of at least two istopes of relative mass 35 and 37 There is no evidence whatever of an individual substance having the atomic weight 35.46. Hence chlorine is to be regarded as a complex element consisting of two principal isotopes of atomic weights 35 and 37 present in such proportion as to afford the mean mass 35.46. The atomic weight of chlorine has been so frequently determined by various observers and by various methods with practically identical results that it seems difficult to believe that it consists of isotopes present in definite and invariable proportion. Mr Aston meets this objection by pointing out that all the accurate determinations have been made with chlorine derived originally from the same source, the sea, which has been perfectly mixed for æons. If samples of the element could be obtained from some other source it is possible that other values of atomic weight would be obtained, exactly as in the case of lead in which the existence of istopes in the metal found in various radioactive minerals was first conclusively established.

Argon, which has an atomic weight of 39.88, was found to consist mainly of an isotope having an atomic weight of 40, associated to the extent of about 3 per cent., with an isotope of atomic weight 36. Krypton and xenon are far more complex. The former would appear to consist of six isotopes, 78, 80, 82, 83, 84, 86; the latter of five isotopes, 129, 131, 132, 134, 136.

Flourine is a simple element of atomic weight 19. Bromine consists of equal quantities of two istopes, 79 and 81. Iodine, on the contrary, would appear to be a simple element of atomic weight 127. The case of tellurium is of special interest in view of its periodic relation to iodine, but the results of its examination up to the present are indefinite.

Boron and silicon are complex elements, each consisting of two isotopes, 10 and 11, and 28 and 29, respectively.

Sulphur, phorphorous, and arsenic are apparently simple elements. Their accepted atomic weights are practically integers.

All this work is so recent that there has been little opportunity, as yet, of extending it to any considerable number of the metallic elements. These, as will be obvious from the nature of the methods employed, present special difficulties. It is, however, highly probable that mercury is a mixed element consisting of many isotopes. These have been partially separated by Brönsted and Hervesy by fractional distillation at very low pressures, and have been shown to vary very slightly in density. Lithium is found to consist of two isotopes, 6 and 7. Sodium is simple, potassium and rubidium are complex, each of the two latter elements consisting, apparently, of two isotopes. The accepted atomic weight of cæsium, 132.81, would indicate complexity, but the mass spectrum shows only one line at 133. Should this be confirmed cæsium would afford an excellent test case. The accepted value for the atomic weight is sufficiently far removed from a whole number to render further investigation desirable.

This imperfect summary of Mr. Aston's work is mainly based upon the account he recently gave to the Chemical Society. At the close of his lecture he pointed out the significance of the results in relation to the Periodic Law. It is clear that the order of the chemical or 'mean' atomic weights in the Periodic table has no practical significance; anomalous cases such as argon and potassium are simply due to the relative proportions of their heavier and lighter isotopes. This does not necessarily invalidate or even weaken the Periodic Law which still remains the expression of a great natural truth. That the expression as Mendeléeff left it is imperfect has long been recognised. The new light we have now gained has gone far to clear up much that was anomalous, especially Moseley's discovery that the real sequence is the atomic number, not the atomic weight. This is one more illustration of the fact that science advances by additions to its beliefs rather than by fundamental or revolutionary changes in them.

The bearing of the electronic theory of matter, too, on Prout's discarded hypothesis that the atoms of all elements were themselves built up of a primordial atom—his *protyle* which he regarded as probably identical with hydrogen—is too obvious to need pointing out. In a sense Prout's hypothesis may be said to be now re-established, but with this essential modification—the primordial atoms he imagined are complex and are of two kinds—atoms of the positive and negative electricty—respectively known as protons and electrons. These, in Mr. Aston's words, are the standard bricks that Nature employs in her operations of element building.

The true value of any theory consists in its comprehensiveness and sufficiency. As applied to chemistry, this theory of 'the inner mechanism of the atom' must explain all its phenomena. We owe to Sir J. J. Thomson its extension to the explantion of the Periodic Law, the atomic number of an element, and of that varying power of chemical combination in an element we term valency. This explanation I give substantially in his own words. The number of electrons in an atom of the different elements has now been determined, and has been found to be equal to the atomic number of the element, that is to the position which the element occupies in the series when the elements are arranged in the order of their atomic weights. We know now the nature and quantity of the materials of which the atoms are made up. The properties of the atom will depend not only upon these factors but also upon the way in which the electrons are arranged in the atom. This arrangement will depend on the forces between the electrons themselves and also on those between the electrons and the positive charges or protons. One arrangement which naturally suggested itself is that the positive charges should be at the centre with the negative electrons around it on the surface of a sphere. Mathematical investigations shows that this is a

possible arrangement if the electrons on the sphere are not too crowded. The mutual repulsion of the electrons resents overcrowding, and Sir J. J. Thomson has shown that when there are more than a certain number of electrons on the sphere, the attraction of a positive charge, limited as in the case of the atom in magnitude to the sum of the charges on the electrons, is not able to keep the electrons in stable equilibrium on the sphere, the layer of electrons explodes and a new arrangement is formed. The number of electrons which can be accommodated on the outer layer will depend upon the law of force between the positive charge and the electrons. Sir J. J. Thomson has shown that this number will be eight with a law of force of a simple type.

To show the bearing of this result as affording an explantion of the Periodic Law, let us, to begin with, take the case of the atom of lithium, which is supposed to have one electron in the outer layer. As each element has one more free electron in its atom than its predecessor, glucinum, the element next in succession to lithium, will have two electrons in the outer layer of its atom, boron will have three, carbon four, nitrogen five, oxygen six, fluorine seven and neon eight. As there cannot be more than eight electrons in the outer layer, the additional electron in the atom of the next element, sodium, cannot find room in the same layer as the other electrons, but will go outside, and thus the atom of sodium, like that of lithium, will have one electron in its outer layer. The additional electron, in the atom of the next element, magnesium, will join this, and the atom of magnesium, like that of glucinum, will have two electrons in the outer layer. Again, aluminium, like boron, will have three; silicon, like carbon, four; phosphorous, like nitrogen, five; sulphur, like oxygen, six; chlorine, like flourine, seven; and argon, like neon, eight. The sequence will then begin again. Thus the number of electrons, one, two, three, up to eight in the outer layer of the atom, will recur periodically as we proceed from one element to another in the order of their atomic weights, so that any property of an element which depends on the number of electrons in the outer layer of its atoms will also recur periodically, which is precisely that remarkable property of the elements which is expressed by the Periodic Law of Mendeléeff, or the Law of Octaves of Newlands.

(To be continued).

## FURTHER NOTES ON ALUMINIUM.

By E. RATTENBURY HODGES

TO my last notes on aluminium acetate (CHEMICAL NEWS, Oct. 8, 1920, p. 178), I would add the three following.

1. Strong acetic acid combines with Al in presence of hydrogen peroxide. At 58° to 60° F., this reaction is completed in four or five days. However, when Al foil is exposed to acid of like strength, in a flask provided with an inverted receiver and heated to boiling point for a few minutes, no chemical change is apparent. After leaving the whole undisturbed for 18 days, the foil was found intact. Removing the receiver, the contents of the flask were left exposed to the air for a week, then, on testing, a small amount of Al acetate was found. To the original acid and foil in the flask, a few drops of hydrogen peroxide were added. In about 30 hours, all the foil had entered into combination. It therefore seems fairly obvious that air or oxygen is essential to the reaction, *i.e.*, oxidation of the base must precede the production of the salt.

2. In Thorpe's Dictionary it is stated that aluminium is vigorously attacked by bromine. I note, however, that with Al foil slightly warmed, this reaction occurs with brilliant incandescence, and evolution of a heavy grey vapour, which is evidently an anhydrous bromide, the solid residue being a dark brown granular deposit of anhydrous aluminium bromide. The latter soon deliquesces to a clear liquid, which after slow evaporation (in air) yielded a crop of fine colourless tabular crystals. Obviously, due precautions had to be taken during the first stages of this observation. Br-water slowly acted upon this foil, yielding, after a few hours, the normal Al bromide. A strong solution of tartaric acid leaves Al unaffected. The same is true of citric acid, but a cold saturated solution of oxalic acid reacted in the course of some weeks, and completely dissolved the foil. On carefully evaporating the resulting oxalate solution, it was found that a portion of the compound formed an oily-looking film, which, on further drying, assumed the colloid state. As the air was slightly humid, the film, after a few minutes exposure, proved to be hygroscopic. A hot solution of oxalic acid steadily acts, but slackens at 57° C., below 30° C. chemical action proceeds feebly.

3. I note a further property of Al; whereas the metal (in foil) is readily attacked by strong phosphoric acid, yielding the resultant phosphate, the concentrated acid fails to act upon tin, even after several weeks' exposure. Hence this reaction with aluminium serves *inter alia* to distinguish it from tin. The action, under certain conditions, of iodine on Al, is noteworthy, but this item must be reserved for a later communication.

## REGULATIONS FOR THE COMPETITIVE SELECTION OF CHEMISTS.

### CLASS II.—IN THE GOVERNMENT LABORATORY.

*Age.*—Candidates must have attained the age of 23 and must not exceed the age of 30 on a date to be fixed in respect of the competition in which they are to take part. A candidate born on the governing date would be admitted on the day he attained the age of 23, but not on the day on which he attained 30.

*Nationality.*—A candidate must be a natural-born British subject, and born of a father also a natural-born British subject; provided that excepton may made in the case of candidates serving in a civil situation to which they were admitted with the certificate of the Civil Service Commissioners, and provided that exception may be made as to the father in the case of candidates who have served in His Majesty's Armed Forces between 4th August, 1914, and 11th November, 1918.

*Military Service.*—Until further order preference will be given to candidates who have served in His Majesty's Forces between 4th August, 1914, and 11th November, 1918.

*Publicity.*—The Government Chemist will take such steps as he thinks appropriate to make known the existence of any vacancy or vacancies which he desires to fill on any one occasion, and the Civil Service Commissioners will satisfy themselves that the steps taken have been such as to secure all desirable publicity

*Application.*—Application shall be made to the Government Chemist, who, after scrutiny of the candidates' credentials, will submit the names of such candidates as appear to have the requiste qualifications for any of the existing or prospective vacancies to the Civil Servce Commissoners, who, if dissatisfied with the number or quality of candidates for any vacancy, may require further search to be made for qualified candidates. Candidates must possess a degree or diploma of a standard not lower than a second class honours degree at a university, and must have had two years' post-graduate experience in chemical work. They should have a working knowledge of technical French and German.

*Health and Character.*—Candidates must satisfy the Civil Service Commissioners as to their health and character. Until further order, and other things being equal, preference will be given by the Selection Board to candidates who are debarred from active employment by a physical impairment due to the war, and not of a nature to interfere with the discharge of the duties of the post

*Competition.* Candidates who pass the scrutiny under Regulation 5 will be admitted to (*a*) an interview before a Selection Board, and (*b*) a written examination in English (the examination in English will include essay writing and précis writing). The Selection Board shall be nominated by the Commissioners in consultation with the authorities of the Department who shall be represented upon it, and, if practicable, one of the Commissioners shall be the Chairman. The Selection Board will take into consideration the candidate's record of experience and education, any recommendations that they may receive from persons named by the candidate as having direct knowledge of his work in the past, the candidate's scientific knowledge, and his personal qualities as shown at the interview; and on their estimation of all the above evidence they will frame their decisions, which will be final. The Selection Board will arrange the candidates in order of merit and the vacancies, will be filled by the appointment of the candidates in order from the list, subject to their passing the examination and satisfying the Commissioners that they are eligible in all respects.

*Warning.*—Any attempt on the part of a candidate to enlist support for his application through Members of Parliament or other influential persons will disqualify him for appointment. The Selection Board will disregard spontaneous recommendations from persons who are not personally acquainted with the candidate's work, whether at school, at the university, in the forces, or otherwise.

*Fee.*—A fee of £5 will be required from each candidate attending the competition.

Salary.—The scale of salaries is at present under consideration by a Committee, and, pending their report, the commencing salary will be £225, with current Civil Service Bonus.

Competitions under these regulations do not take place at fixed intervals, but are held from time to time on the occurrence of vacancies. No date has at present been fixed for any competition under these regulations, which are liable to alteration from time to time.

## NOTES.

At the invitation of the General Manager of the Great Eastern Railway we have been able to make a practical test of their new route to Belgium and the Continent, via Harwich and Zeebrugge. For any hard-worked professional man with but little time to spare the route offers many inducements. The Railway Company has made arrangements by which it is possible to visit Zeebrugge, Bruges, Ghent, Brussels, Antwerp, and the battle area, easily and at a very small expense. It is now possible to leave Liverpool Street Station in the evening and be bowled down to Harwich in a fast train, where a splendid boat waits to take you across to Zeebrugge. from whence a good service of trains makes it easy to travel to any part of Belgium. For ourselves we started at 8 p.m. on Monday, visited Zeebrugge, Bruges, Ghent, Ypres Roulers, Courtrai, Ostend, Blankenburghe, and thoroughly explored the historic Mole of Zeebrugge, recrossing comfortably on Thursday night, and were back at the Office before 9 a.m. on Friday. Railway travelling is cheap in Belgium, and with the exchange at 49 the charges seem ridiculously small; the officials are most obliging and the language presents no difficulty, as nearly everyone knows a little English. The Great Eastern Railway Company also run a special "Sunday in Belgium" trip, the train leaving London on Saturday night, giving a full day in Belgium and enabling one to be home by 8 a.m. on Monday. By this trip it is possible to go inland or to visit Ostend and any of the seaside towns easily as there is good electric train service right along the coast. For this trip no passport is necessary and the return fare is only £2 10s. second class and £3 15s. first. We can recommend the Harwich-Zeebrugge service as affording an easy and economical relief from the worry and pressure of London, and it at least enables one to contrast the unrest and unemployment agitation at home with the quiet industry and labour that is going on in that sorely abused little country across the water

The Sir John Cass Technical Institute. The new session of the Sir John Cass Technical Institute, Aldgate, E.C.3, will commence on Monday, September 26th. Students will be enrolled during the previous week commencing Monday, September 19th, between 7 and 9 p.m. The courses of instruction at the Institute are especially directed to the technical training of those engaged in chemical, metallurgical, and electrical industries and in the trades associated therewith. Full facilities are provided in the well-equipped laboratories of the Institute for special investigations and research. The instruction in experimental science also provides systematic courses for the examinations of London University and of the Institutes of Physics and Chemistry. Special courses of higher technologi-

cal instruction form a distinctive feature of the work of the Institute. For the forthcoming session these include courses on the Fermentation Industries, Glass Technology, Colloids, Metallography and Pyrometry, Heat Treatment and Mechanical Testing of Metals and Alloys. An important development for the new session is the establishment of courses of instruction in Petroleum Technology. These have been arranged in consultation with representatives of the chief oil companies and have been designed to meet the requirements of those engaged in or associated with the practical and scientific control of the petroleum industry In view of the fact that most of the chief oil companies have their offices and several have their laboratories in the immediate district, the Institute is very favourably situated for this branch of instruction, which it is anticipated will form a most valuable extension of the work of the Institute. The leading oil companies have very generously contributed towards the establishment of this department of petroleum technology.

IS AMERICA LEADING BRITISH INDUSTRIES?—*In* the current issue of the *Industrial League and Council Journal*, Mr. E. J. P. Benn, who has recently returned from America, gave his impressions of labour and industry in that country. On the question of social legislation, he said:—"Imagine a humble student of social problems, searching through a distant land, endeavouring to find someone with whom he could discuss intelligently such elementary matters as Old Age Pensions, Health Insurance, Unemployment Pay, or even Poor Law itself. Imagine a land with 110 million civilized persons without a political Labour Party, and with, so far as I am able to judge, no earthly chance of ever getting one. Imagine a land in which even the workers never heard the word 'ca-canny', and regard restriction of output as a mythical madness that does not really exist." On the status of the workers, he remarked:—'It is frequently said that America is fifty years behind us in matters of social reform, and particularly in Labour organization. I had the advantage of three long talks with that veteran leader, Sam Gompers, and I put that point to him. Mr. Gompers was indignant, and claimed that so far from being fifty years behind us, the United States of America are 100 years ahead of us. He claims that the true test of success of a Labour movement is not to be found in the violence of its political programme; there is a more serious, a more effective test. Go to the homes of the people; look at the social and economic status of the wokers. He points with pride to the six million working-class homes which are either completely or partly owned by their workman occupants. He called my attention to the 12 million automobiles among the 110 million people; sufficient at a pinch to move the whole population at one go. It is stated that there are no less than 15 million owners of shares, stock or some form of property among the citizens of the United States. America, like the rest of the world, is having her revolution, but it is a very different revolution from any of the many brands that we are familiar with in Europe. The revolution in America is taking the form of the transference of large blocks of industrial capital into the hands of the workers in industry." As a general comparison of America and Britain as regards Industry and Commerce, he said: "In a word, the whole force of public opinion in America is directed to teaching its people how to *push*. Our opinion on the contrary seems to be with teaching its people how to *lean*" A general review of the activities of the Whitley Councils and reviews of industrial books makes up a very interesting magazine.

RAINFALL.—The mean rainfall during May at 12 stations which have been selected as giving equal representation for all parts of the Thames Basin was 1·60in., being 0·33 of an inch below the average mean rainfall for that month during the previous 38 years. The average daily natural flow of the Thames at Teddington Weir during the month was 481·9 million gallons, being 653·8 million gallons below the daily average for the 38 preceding years. The maximum daily flow was 753·1, and the minimum 260·3 million gallons.

APPARATUS FOR MANUFACTURE OF ETHER AND STRAY ELECTRIC CURRENTS.—The deterioration, often very considerable, of the leaden apparatus employed for the manufacture of crude ether is due, as we know, to the formation of electric currents. These are produced, for example, in the case when the worm is made of hard lead whilst the still is of soft lead. It has, in fact, been noted that with a hard lead cathode, a soft lead anode, and, as electrolyte, a mixture of alcohol and sulphuric acid, such as that utilised for manufacture of ether, an electric current is produced. At the ordinary temperatures, a current of 0·05 ampere, with a difference of potential of 0·1 to 0·2 volt has been noted· usually the current does not exceed 0·01 ampere. To decrease wear of the plant, a writer in the *Chemiker Zeitung* recommends the use of very pure lead. All parts of the plant must be made with lead of uniform composition. Finally, the plant should be connected with the ground in various points.—*Chimie et Industrie*, July, 1921.

## NEW COMPANIES.

The under-mentioned particulars of New Companies recently registered are taken from the Daily Register compiled by JORDAN & SONS, LIMITED, Company Registration Agents, Chancery Lane, W.C.2.

J. P. DAWE & COMPANY, LIMITED.—(176465)—Registered August 25th, 1921. 81, Malden Road, Kentish Town, N.W. To carry on the business of Chemists and Druggists. Nominal Capital: £500 in 500 Shares of £1 each. Directors: R. J. P. Dawe, 35, Junction Road, Holloway, N.; Ada H. Dawe, 35, Junction Road, Holloway, N. Qualification of Directors: £1 Remuneration of Directors: To be voted by Company.

BURLINGTON INDUSTRIAL LABORATORIES, LIMITED.—(176443)—Registered August 24th, 1921. To carry on the business of Analytical, Consulting and Manufacturing Chemists. Nominal Capital: £1,000 in 1,000 Shares of £1 each. Directors: F. Goddard, 78, Pershore Road Thornton Heath, Surrey; H. Elliott, 7, Crawford Avenue, Bolton, Lancashire. Qualification of Directors: £50. Remuneration of Directors: To be voted by Company.

TIMMIS & INGHAM, LIMITED.—(176453)—Registered August 24th, 1921. 102, High Road, Ilford. To carry on the business of Chemical Manufacturers and Dealers. Nominal Capital: £4,000 in 4,000 Shares of £1 ach. Directors: G. Ingham, 102, High Road, Ilford; C H. Cooper, 199, Balfour Road, Ilford (Permanent Directors). Remuneration of Directors: £312 per annum each Permanent Directors.

Roberts (Barking), Limited.—(176473)—Registered August 25th, 1921. Creekmouth, Barking, Essex. To carry on the business of Manufacturers and Dealers in Inks, Paints, Varnishes, Oils and Colours. Nominal Capital: £100 in 100 Shares of £1 each. Directors: R. W. Orrock, "Bleak House", Creekmouth, Barking (Managing Director and Chairman), H. P. Orrock, 51, Salisbury Avenue, Barking, E. Clarke, 8, Lady Margaret Road, Kentish Town, N.W. Qualification of Directors: £2. Remuneration of Directors: To be voted by Company.

## New Patents.

This List is specially compiled for the *Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, W.C. 2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

21708—British Dyestuffs Corporation, Ltd.—Manufacture of solnble acid colouring-matters and intermediate compounds for manufacture thereof. August 16.

21881—Chemische Fabric Rhenania, o.—Process for manufacture of sulphur from sulphuretted hydrogen. August 17.

22027—Herzog, E.—Manufacture of sodium peroxide. August 19.

21763—Wolvekamp, M. E.—Alkali salts of oxidizied protalbinic and lysalbinic acid as stable protective colloids for mercury compounds. August 16.

21649—Varwerke, vorm. Meister, Lucius and Brunning—Process of preparing aliphatic dialkylaminoalkyl compounds. August 15.

21852—Bate, S. C.—Manufacture of triarylmethane colouriug matters.

*Specifications published this Week.*

167540—South Metropolitan Gas Co. and Parrish, P.—Manufacture of ammonium sulphide.

167555—Matheson, A.—Manufacture of alum and sulphate of alumina.

149667—Pfannenschmidt, P. E.—Acid chambers, acid towers, acid mains and similar arrangements.

*Abstract Published this Week.*

*Hydrocarbons.*—Patent No. 165452.—Mr. C. Weizmann, of 41, Campden House Road, Kensington and D. A. Legg, of 15, Sisters Avenue, North Side, Clapham Common, both in London, have obtained a Patent for an improved process for obtaining hydrocarbons of the naphthene series. They are prepared by polymerizing 2- or 3-butene or mixture thereof by means of anhydrous aluminium chloride; the butene may be treated in the gaseous or liquefied condition and the polymerization may be effected at a low temperature, or at ordinary temperature under pressure.

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# BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

EDINBURGH, 1921.

## INAUGURAL ADDRESS OF THE PRESIDENT.

SIR T. EDWARD THORPE, C.B., D.Sc., Sc.D., LLD., F.R.S., Hon. F.R.S. Edin.

(Concluded from p. 141).

THE valency of the elements, like their periodicity, is a consequence of the principle that equilibrium becomes unstable when there are more than eight electrons in the outer layer of the atom. For on this view the chemical combination between two atoms, A and B, consists in the electrons of A getting linked up with those of B. Consider an atom like that of neon, which has already eight electrons in its outer layer; it cannot find room for any more, so that no atoms can be linked to it, and thus it cannot form any compounds. Now take an atom of fluorine, which has seven electrons in its outer layer; it can find room for one, but only one, electron, so that it can unite with one, but not with more than one, atom of an element like hydrogen, which has one electron in the outer layer. Fluorine, accordingly, is monovalent. The oxygen atom has six electrons; it has, therefore, room for two more, and so can link up with two atoms of hydrogen: hence oxygen is divalent. Similarly nitrogen, which has five electrons and three vacant places, will be trivalent, and so on. On this view an element should have two valencies, the sum of the two being equal to eight. Thus, to take oxygen as an example, it has only two vacant places, and so can only find room for the electrons of two atoms; it has, however, six electrons available for filling up the vacant places in other atoms, and as there is only one vacancy to be filled in a fluorine atom the electrons in an oxygen atom could fill up the vacancies in six fluorine atoms, and thereby attach these atoms to it. A fluoride of oxygen of this composition remains to be discovered, but its analogue, $SF_6$, first made known by Moissan, is a compound of this type. The existence of two valencies for an element is in accordance with views put forward some time ago by Abegg and Bödlander. Prof. Lewis and Mr. Irving Longmuir have developed, with great ingenuity and success, the consequences which follow from the hypothesis that an octet of electrons surrounds the atoms in chemical compounds.

The term "atomic weight" has thus acquired for the chemist an altogether new and much wider significance. It has long been recognised that it has a far deeper import than as a constant useful in chemical arithmetic. For the ordinary purposes of quantitative analysis, of technology, and of trade, these constants may be said to be now known with sufficient accuracy. But in view of their bearing on the great problem of the essential nature of matter and on the "superlatively grand question: What is the inner mechanism of the atom?" they become of supreme importance. Their determination and study must now be approached from entirely new standpoints and by the conjoint action of chemists and physicists. The existence of isotopes has enormously widened the horizon. At first sight it would appear that we should require to know as many atomic weights as there are isotopes, and the chemist may well be appalled at such a prospect. All sorts of difficulties start up to affright him, such as the present impossibility of isolating isotopes in a state of individuality, their possible instability, and the inability of his quantitative methods to establish accurately the relatively small differences to be anticipated. All this would seem to make for complexity. On the other hand, it may eventually tend towards simplification. If, with the aid of the physicist we can unravel the nature and configuration of the atom of any particular element, determine the number and relative arrangement of the constituent protons and electrons, it may be possible to arrive at the atomic weight by simple calculation, on the assumption that the integer rule is mathematically valid. This, however, is almost certainly not the case, owing to the influence of "packing." The little differences, in fact, may make all the difference. The case is analogous to that of the so-called gaseous laws in which the departures from their mathematical expression have been the means of elucidating the physical constitution of the gases and of throwing light upon such variations in their behaviour as have been observed to occur. There would appear, therefore, ample scope for the chemist in determining with the highest attainable accuracy the departures from the whole-number rule, since it is evident that much depends upon their exact extent.

These considerations have already engaged the attention of chemists. For some years past, a small International Committee, originally appointed in 1903, has made and published an annual report in which they have noted such determinations of atomic weight as have been made during the year preceding each report, and they have from time to time made suggestions for the amendment of the Tables of Atomic Weights, published in text-books and chemical journals, and in use in chemical laboratories. In view of recent developments, the time has now arrived when the work of this International Committee must be reorganised and its aims and functions extended. The mode in which this should be done has been discussed at the meeting in Brussels, in June last, of the International Union of Chemistry Pure and Applied, and has resulted in strengthening the constitution of the Committee and in a wide extension of its scope.

The crisis through which we have recently passed has had a profound effect upon the world. The spectacle of the most cultured and most highly developed peoples on this earth, armed with every offensive appliance which science and the inventive skill and ingenuity of men could suggest, in the throes of a death struggle must have made the angels weep. That dreadful

harvest of death is past, but the aftermath remains. Some of it is evil, and the evil will persist for, it may be, generations. There is, however, an element of good in it, and the good, we trust, will develop and increase with increase of years. The whole complexion of the world—material, social, economic, political, moral, spiritual—has been changed, in certain aspects immediately for the worse, in others prospectively for the better. It behoves us, then, as a nation, to pay heed to the lessons of the war.

The theme is far too complicated to be treated adequately within the limits of such an address as this. But there are some aspects of it germane to the objects of this Association, and I venture, therefore, in the time that remains to me, to bring them to your notice.

The Great War differed from all previous internecine struggles in the extent to which organised science was invoked and systematically applied in its prosecution. In its later phases, indeed, success became largely a question as to which of the great contending parties could most rapidly and most effectively bring its resources to their aid. The chief protagonists had been in the forefront of scientific progress for centuries, and had accumulated experience of the manifold applications of science in practically every department of human activity that could have any possible relation to the conduct of the war. The military class in every country is probably the most conservative of all the professions and the slowest to depart from tradition. But when nations are at grips, and they realise that their very existence is threatened, every agency that may tend to cripple the adversary is apt to be resorted to—no matter how far it departs from the customs and conventions of war. This is more certain to be the case if the struggle is protracted. We have witnessed this fact in the course of the late War. Those who, realising that in the present imperfect stage of civilisation, wars are inevitable, and yet strove to minimise their horrors, and who formulated the Hague Convention of 1899, were well aware how these horrors might be enormously intensified by the applications of scientific knowledge, and especially of chemistry. Nothing shocked the conscience of the civilised world more than Germany's cynical disregard of the undertaking into which she had entered with other nations in regard, for instance, to the use of lethal gas in warfare. The nation that treacherously violated the Treaty of Belgium, and even applauded the action, might be expected to have no scruples in repudiating her obligations under the Hague Convention. April 25, 1915, which saw the clouds of the asphyxiating chlorine slowly wafted from the German trenches towards the lines of the Allies, witnessed one of the most bestial episodes in the history of the Great War. The world stood aghast at such a spectacle of barbarism. German *kultur* apparently had absolutely no ethical value. Poisoned weapons are employed by savages, and noxious gas had been used in Eastern warfare in early times, but its use was hitherto unknown among European nations. How it originated among the Germans—whether by the direct unprompted action of the Higher Command, or, as is more probable, at the instance of persons connected with the great manufacturing concerns in Rhineland, has, so far as I know, not transpired. It was not so used in the earlier stages of the War, even when it had become a war of position. It is notorious that the great chemical manufacturing establishments of Germany had been, for years previously, sedulously linked up in the service of the war which Germany was deliberately planning—probably, in the first instance, mainly for the supply of munitions and medicaments. We may suppose that it was the tenacity of our troops, and the failure of repeated attempts o dislodge hem by direct attack, that led to the employment of such foul methods. Be this as it may, these methods became part of the settled practice of our enemies, and during the three succeeeding years, that is from April, 1915, to September, 1918, no fewer than eighteen different forms of poison—gases, liquids, and solids—were employed by the Germans. On the principle of Vespasian's law, reprisals became inevitable, and for the greater part of three years we had the sorry spectacle of the leading nations of the world flinging the most deadly products at one another that chemical knowledge could suggest and technical skill contrive. Warfare, it would seem, has now definitely entered upon a new phase. The horrors which the Hague Convention saw were imminent, and from which they strove to protect humanity, are now, apparently, by the example and initiative of Germany, to become part of the established procedure of war. Civilisation protests against a step so retrograde. Surely comity among nations should be adequate to arrest it. If the League of Nations is vested with any real power, it should be possible for it to devise the means, and to ensure their successful application. The failure of the Hague Convention is no sufficient reason for despair. The moral sense of the civilised world is not so dulled but that, if roused, it can make its influence prevail. And steps should be taken without delay to make that influence supreme, and all the more so that there are agencies at work which would seek to perpetuate such methods as a recognised procedure of war. The case for what is called chemical warfare has not wanted for advocates. It is argued that poison gas is far less fatal and far less cruel than any other instrument of war. It has been stated that "amongst the 'mustard gas' casualties the deaths were less than 2 per cent, and when death did not ensue complete recovery generally utimately resulted. . . . Other materials of chemical warfare in use at the Armistice do not kill at all; they produce casualties which, after six weeks in hospital, are discharged practically without permanent hurt." It has been argued that, as a method of conducting war, poison-gas is more humane than preventive medicine. Preventive medicine has increased the unit dimension of an army, free from epidemic and communicable disease, from 100,000 men to a million. "Preventive medicine has made it possible to maintain 20,000,000 men under arms and abnormally free from disease, and so provided greater scope for the killing activites of the other military weapons. . . . Whilst the surprise effects of chemical warfare aroused anger as being contrary to military tradition, they were minute compared with those of preventive medicine. The former slew in its thousands, whilst the latter slew its millions and is still reaping the harvest." This argument carries no conviction. Poison gas is not

merely contrary to European military tradition; it is repugnant to the right feeling of civilised humanity. It in no wise displaces or supplants existing instruments of war, but creates a new kind of weapon, of limitless power and deadliness. 'Mustard gas' may be a comparatively innocuous product as lethal substances go. It certainly was not intended to be such by our enemies. Nor, presumably, were the Allies any more considerate when they retaliated with it. Its effects indeed, were sufficiently terrible to destroy the German *moral*. The knowledge that the Allies were preparing to employ it to an almost boundless extent was one of the factors that determined our enemies to sue for the Armistice. But if poisonous chemicals are henceforth to be regarded as a regular means of offence in warfare, is it at all likely that their use will be confined to 'mustard gas,' or indeed to any other of the various substances which were employed up to the date of the Armistice? To one who, after the peace, inquired in Germany concerning the German methods of making 'mustard gas,' the reply was :—'Why are you worrying about this when you know perfectly well that this is not the gas we shall use in the next war?' "

I hold no brief for preventive medicine, which is well able to fight its own case. I would only say that it is the legitimate business of preventive medicine to preserve by all known means the health of any body of men, however large or small, committeed to its care. It is not to its discredit if, by knowledge and skill, the numbers so maintained run into millions instead of being limited to thousands. On the other hand, "an educated public opinion" will refuse to give credit to any body of scientific men who employ their talents in devising means to develop and perpetuate a mode of warfare which is abhorrent to the higher instincts of humanity.

This Association, I trust, will set its face against the continued degradation of science in thus augmenting the horrors of war It could have no loftier task than to use its great influence in arresting a course which is the very negation of civilisation.

## THE LABORATORY OF THE LIVING ORGANISM.

ADDRESS DELIVERED BEFORE SECTION B (CHEMISTRY)

BY M. O. FORSTER, D.Sc., F.R.S., President of the Section.

MANY and various are the reasons which have been urged, at different periods of its history, for stimulating the study of chemistry. In recent years these have been either defensive or frankly utilitarian, in the latter feature recalling the less philosophic aspects of alchemy; moreover, it is to be feared that a substantial proportion of those who have lately hastened to prepare themselves for a chemical career have been actuated by this inducement. It is the duty, therefore, of those who speak with any degree of experience to declare that the only motive for pursuing chemistry which promises anything but profound disappointment is an affection for the subject sufficiently absorbing to displace the attraction of other pursuits. Even to the young chemist who embarks under this inspiration the prospect of success as recognised by the world is indeed slender, but, as his knowledge grows and the consequent appreciation of our ignorance widens, enthusiasm for the beauty and mystery of surrounding nature go far in compensating for the disadvantages of his position. On the other hand, he who has been beguiled into embracing chemistry on the sole ground of believing it to be a "good thing" will either desert it expeditiously or almost surely starve and shower purple curses upon his advisers.

In one respect chemistry resembles measles—every boy and girl should have it, lest an attack in later life should prove more serious. Moreover, whilst it is not only unnecessary, but most undesirable, to present the subject as if every boy and girl were going to be a chemist, it is most important to present it in such a manner that every educated citizen may realise the intimate part which chemistry plays in his daily life. Not only do chemical principles underlie the operations of every industry, but every human being—indeed, every living plant and animal—is, during each moment of healthy life, a practical organic and physical chemist, conducting analytical and synthetical processes of the most complex order with imperturbable serenity. No other branch of knowledge can appeal for attention on comparable grounds; and without suggesting that we should all, individually, acquire sufficient chemical understanding fully to apprehend the changes which our bodies effect so punctually and so precisely—for this remains beyond the power of trained chemists—it may be claimed that an acquantaince with the general outlines of chemistry would add to the mental equipment of our people a source of abundant intellectual pleasure which is now unfairly denied them. We have been told that the world shall be made a fit place for heroes to live in; but is not the preliminary to this ideal an exposition to those heroes of the wonder and beauty of the world which they already occupy, on the principle that if you cannot have what you like, it is elementary wisdom to like what you have? In following the customary practice of surveying matters of interest which have risen from our recent studies, therefore, it is the purpose of this address to emphasise also those æsthetic aspects of chemistry which offer ample justification for the labour which its pursuit involves.

What is breakfast to the average man? A hurried compromise between hunger and the newspaper. How does the chemist regard it? As a daily miracle which gains, rather than loses, freshness as the years proceed. For just think what happens. Before we reach the table, frizzled bacon, contemplated or smelt, has actuated a wonderful chemical process in our bodies. The work of Pavlov has shown that if the dog has been accustomed to feed from a familiar bowl the sight of that bowl, even empty, liberates from the appropriate glands a saliva having the same chemical composition as that produced by snuffing the food. This mouth-watering process, an early experience of childhood, is known to the polite physiologist as a "psychic reflex," and the various forms assumed by psychic reflex, responding to the various excitations which arise in the daily life of a human

being, must be regarded by the chemical philosopher as a series of demonstrations akin to those which he makes in the laboratory, but hopelessly inimitable with his present mental and material resources. For, extending this principle to the other chemical substances poured successively into the digestive tract, we have to recognise that the minute cells of which our bodies are co-ordinated assemblages possess and exercise a power of synthetic achievement contrasted with which the classical syntheses, occasionally enticing the modern organic chemist to outbursts of pride, are little more than hesitating preliminaries. Such products of the laboratory, elegant as they appear to us, represent only the fringe of this vast and absorbing subject. Carbohydrates, alkaloids, glucosides, and purines, complex as they seem when viewed from the plane of their constituent elements, are but the molecular debris strewing the path of enzyme action and photochemical synthesis, whilst the enzymes produced in the cells, and applied by them in their ceaseless metamorphoses, are so far from having been synthesised by the chemist as to have not even yet been isolated in purified form, although their specific actions may be studied in the tissue-extracts containing them.

Reflect for a moment on the specific actions. The starch in our toast and porridge, the fat in our butter, the proteins in our bacon, all insoluble in water, by transformations otherwise unattainable in the laboratory are smoothly and rapidly rendered transmissible to the blood, which accepts the products of their disintegration with military precision. Even more amazing are the consequences. Remarkable as the foregoing analyses must appear, we can dimly follow their progress by comparison with those more violent disruptions of similar materials revealed to us by laboratory practice, enabling such masters of our craft as Emil Fischer to isolate the resultant individuals. Concurrently with such analyses, however, there proceeds syntheses which we can scarcely visualise, much less imitate. The perpetual elaboration of fatty acids from carbohydrates, of proteins from amino-acids, of zymogens and hormones as practised by the living body are beyond the present comprehension of the biochemist; but their recognition is his delight, and the hope of ultimately realising such marvels provides the dazzling goal towards which his efforts are directed.

*The Vegetable Alkaloids.*

The joyous contemplation of these wonders is an inalienable reward of chemical study, but it is denied to the vast majority of our people. The movements of currency exchange, to which the attention of the public has been directed continuously for several years, are clumsy contortions compared with the chemical transformations arising from food exchange. It should not be impossible to bring the skeleton of these transformations within the mental horizon of those who take pleasure in study and reflection; and to those also the distinction between plants and animals should be at least intelligible. The wonderful power which plants exercise in building up their tissues from carbonic acid, water, and nitrogen, contrasted with the powerlessness of animals to utilise these building materials until they have been already assembled by plants, is a phenomenon too fundamental and illuminating to be withheld, as it now is, from all but the few. For by its operation the delicate green carpet, which we all delight in following through the annual process of covering the fields with golden corn, is accomplishing throughout the summer months a vast chemical synthesis of starch for our benefit. Through the tiny pores in those tender blades are circulating freely the gases of the atmosphere, and from those gases—light, intangible nothingness, as we are prone to regard them—this very tangible and important white solid compound is being elaborated. The chemist cannot do this. Plants accomplish it by their most conspicuous feature, greenness, which enables then to put solar energy into cold storage; they are accumulating fuel for subsequent development of bodily heat energy. Side by side with starch, however, these unadvertised silent chemical agencies elaborate molecules even more imposing, in which nitrogen is interwoven with the elements of starch, and thus are produced the vegetable alkaloids.

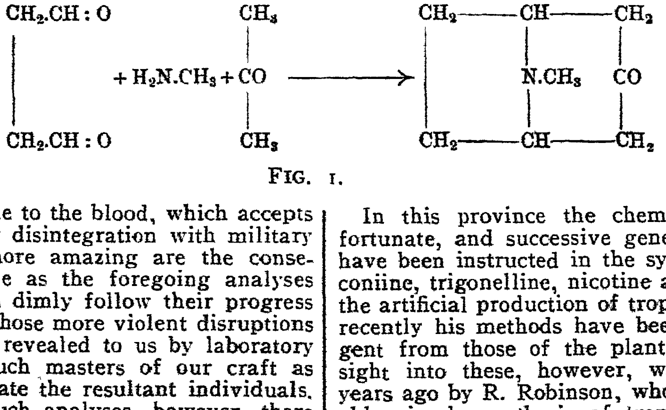


FIG. 1.

In this province the chemist has been more fortunate, and successive generations of students have been instructed in the synthesis of piperine, coniine, trigonelline, nicotine and extensions from the artificial production of tropine; but until quite recently his methods have been hopelessly divergent from those of the plant. Enlightening insight into these, however, was given just four years ago by R. Robinson, who effected a remarkably simple synthesis of tropinone by the mere association of succindialdehyde, methylamine, and acetone in water, unassisted by a condensing agent or an increase of temperature (see Fig. 1).

Although the yield was very small, it reached 42 per cent when acetone was replaced by a salt of its dicarboxylic acid, which might easily arise from citric acid as one of the itermediate compounds used by plants in their synthetical exercises.

Based upon this experiment, R. Robinson (1917) has developed an attractive explanation of the phytochemical synthesis of alkaloids, in which the genesis of a pyrrolidine, piperidine, quinuclidine, or *iso*-quinoline group is shown to be capable of proceeding from the association and interaction of an amino-acid, formaldehyde, acetonedicarboxylic acid and the intermediate products of these, taking place under the influence of oxidation, reduction, and condensation such as the plant is known to effect. It would be scarcely

be fair to the resourceful skill embodied in this theory to attempt an abbreviated description of the methods by which molecules as complex even as those of morphine and narcotine may be developed. Ornithine ($\alpha\delta$-diaminovaleric acid) is represented as the basis of hygrine, cuschygrine, and the tropine alkaloids, whilst the coniine group may spring from lysine ($\alpha\epsilon$-diaminocaproic acid). A particularly interesting application of these principles has been made with reference to the vital synthesis of harmine, which W. H. Perkin and R. Robinson (1919) represent as arising from a hydroxytryptophan as yet undiscovered; meanwhile they have shown that harman is identical with the base obtained by Hopkins and Cole on oxidising tryptophan itself with ferric chloride. Thus it may be claimed that Robinson's theory represents a notable advance in our conception of these vital changes, and that by means of the carbinolamine and aldol condensations involved fruitful inquiries into constitution and the mechanism of synthesis will follow.

### *The Nucleic Acids.*

Owing to the venerable position occupied by alkaloids in the systematic development of chemical science, and to the success which has attended elucidation of their structure, many of us have become callous to the perpetual mystery of their elaboration. Those who seek fresh wonders, however, need only turn to the nucleic acids in order to satisfy their curiosity. For in the nucleic acid of yeast the chemist finds a definite entity forming a landmark in the path of metabolic procedure, a connecting link between the undefined molecules of living protein and the crystallisable products of katabolic disintegration.

Let us review this remarkable substance. With an empirical formula, $C_{38}H_{49}O_{29}N_{15}P_4$, it has a molecular weight (1303) exceeding that of the octadecapeptide (1213) synthesised by Fischer (1907), although considerably below those of the penta-(penta-acetyl-*m*-digalloyl)-$\beta$-glucose (2136) produced by Fischer and Bergmann (1918), and of the hepta-(tribenzoylgalloyl)-*p*-iodophenylmaltosazone (4021) elaborated by Fischer and Freudenberg (1912). Nevertheless, its intrinsic importance is transcendent. In the language of chemistry it is a combination of four nucleotides, linked with one another through the pentose molecule, *d*-ribose, which is common to each, and owing its acid character to phosphoric acid, also common to the component nucleotides. The latter differ from one another in respect of their nitrogenous factors, which are guanine (2-amino-6-oxypurine), adenine (6-aminopurine), uracil (2 : 6-dioxypyrimidine), and cytosine (2-oxy-6-aminopyrimidine), giving their names to the four nucleotides linked with each other in the following manner:

$$
\begin{array}{lr}
(HO)_2PO.O.C_5H_7O_2.C_5H_4ON_5 & \text{(guanine)} \\
\qquad\qquad\quad | & \\
\qquad\qquad\quad O & \\
\qquad\qquad\quad | & \\
(HO)_2PO.O.C_5H_8O.C_4H_4ON_3 & \text{(cytosine)} \\
\qquad\qquad\quad | & \\
\qquad\qquad\quad O & \\
\qquad\qquad\quad | & \\
(HO)_2PO.O.C_5H_8O.C_5H_4N_5 & \text{(adenine)} \\
\qquad\qquad\quad | & \\
\qquad\qquad\quad O & \\
\qquad\qquad\quad | & \\
(HO)_2PO.O.C_5H_7O_2.C_4H_3O_2N_2 & \text{(uracil)}
\end{array}
$$

We owe this picture of plant nucleic acid to the combined researches of many chemists, conspicuous amongst whom is A. Kossel; he derived purine bases from nucleins in the early eighteen-eighties, and subsequently identified the products of completely hydrolysing the nucleic acids from yeast and from the thymus gland. Characterisation of intermediate products in such hydrolyses—namely, the nucleotides of guanine, cytosine, adenine, and uracil—with the corresponding nucleosides, guanosine, cytidine, adenosine, and uridine, is due chiefly to W. Jones and to P. A. Levene, with who was later associated W. A. Jacobs; but the most picturesque of all contributions to the subject was made by the earliest of the systematic investigators, Friedrich Miescher, who followed his isolation of nuclein (nucleic acid) from pus cells (1868) by the remarkable discovery that the spermatozoa heads of Rhine salmon consist almost entirely of protamine nucleate (1874), and that this must have arisen, not directly from food, but from muscle protein.

Whilst the yeast cell and the wheat embryo have the power to synthesise nucleic acid of the structure represented above, the thymus gland elaborates another nucleic acid in which a hexose is substituted for *d*-ribose, and uracil is replaced by thymine, its methyl derivative (5-methyl-2 : 6-dioxypyrimidine); the order and mode of nucleotide linkage are also different. These nucleic acids, although deriving their carbohydrate and phosphoric acid from the nourishment on which the organism thrives, do not owe the purine factors to the same source; in other words, the tissues must have power to synthesise a purine ring. The mechanism by which they exercise this power is one of the many problems which await elucidation but arginine ($\alpha$-amino-$\delta$-guanidinevaleric acid) has been indicated as one possible origin, whilst histidine ($\alpha$-amino-$\beta$-imidazolylpropionic acid) may be a source of the pyrimidine nucleus.

The transformations undergone by nucleic acid in contact with tissue-extracts have provided the subjects of numerous investigations extending over thirty years. In fact, the experimental materials of such voluminous complexity as to be unintelligible without the guidance of an expert, and in this capacity W. Jones has rendered valuable service by his recent lucid arrangement of the subject (1921). From this it is comparatively easy to follow the conversion of nucleic acid into uric acid through the agency of enzymes, and a review of these processes can only serve to increase our admiration for the precision and facility with which the chemical operations of the living body are conducted. Regarding for the sake of simplicity only the purine nucleotides, these are probably the first products of hydrolysing nucleic acid, and from them there may be liberated either phosphoric acid by a phosphonuclease, or the purine-base by a purine-nuclease, giving rise to guanine and adenine, with their nucleosides, guanosine and adenosine. Thereafter the procedure is less obscure. The four products exchange their amino-group for hydroxyl under the influence of their respective deaminase—namely, guanase, adenase, guanosine-deaminase or adenosine-deaminase. The two original nucleosides, with their corresponding derivatives, xanthosine and inosine, are then hydrolysed by

their appropriate hydrolase, and the resulting oxypurines, xanthine and hypoxanthine, are further oxidised by xanthine-oxidase to uric acid. This is the concluding phase of purine metabolism in man and apes, but other animals are able to transform uric acid into allantoin by means of uricase. The changes may be represented diagrammatically (see Fig. 2).

Considerable progress has been made also in localising the various enzymes among the organs of the body, particularly those of animals. Into the results of these inquiries it is not the purpose of this address to enter further than to indicate that they reveal a marvellous distributon, throughout the organism, of materials able to exert at the proper moment those chemical activities appropriate to the changes which they are required to effect. The contemplation of such a system continuously, and in health unerringly, completing a series of chemical changes so numerous and so diverse, must produce in every thoughtful mind a sensation of humble amazement. The aspect of this miraculous organisation which requires most to be emphasised, however, is that an appreciation of its complex beauty can be gained only by those to whom at least the elements of a training in chemistry have been vouchsafed. Such training has potential value from an ethical standpoint, for chemistry is a drastic leveller; in the nucleic acids man discovers a kinship with yeast-cells, and in their common failure to transform uric acid into allantoin he finds a fresh bond of sympathy with apes. The overwhelming majority of people arrive at the grave, however, without having had the slightest conception of the delicate chemical machinery and the subtle physical changes which, throughout each moment of life, they have methodically and unwittingly operated.

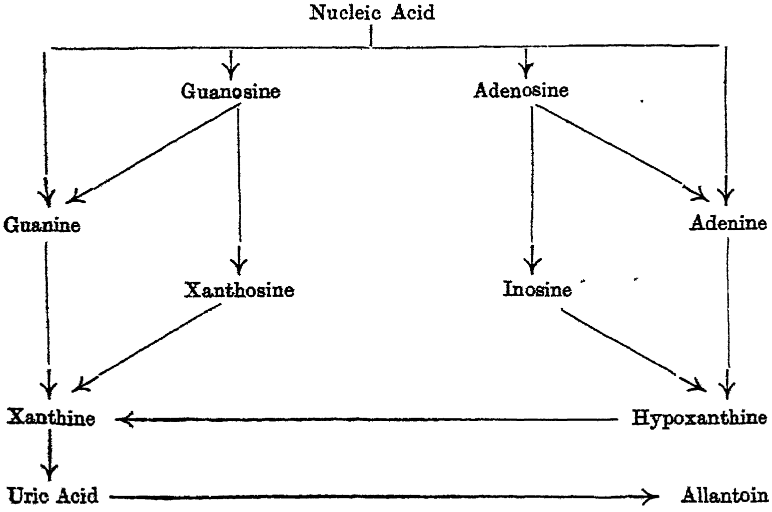



FIG. 2.

*Chlorophyll and Hæmoglobin.*

To those who delight in tracing unity among the bewildering intricacies of natural processes, and by patient comparison of superficially dissimilar materials triumphantly to reveal continuity in the discontinuous, there is encouragement to be found in the relationship between chlorophyll and hæmoglobin. Even the most detached and cynical observer of human failings must glow with a sense of worship when he perceives this relationship, and thus brings himself to acknowledge the commonest of green plants among his kindred. Because, just as every moment of his existence depends upon the successful performance of its chemical duties by the hæmoglobin of his blood corpuscles, so the life and growth of green plants hinge on the transformations of chlorophyll.

The persevering elucidation of chlorophyll structure ranks high in the achievements of modern organic chemistry, and in its later stages is due principally to Willstätter and his collaborators, whose investigations culminated in 1913. Eliminating the yellow and colourless companions of the substance by a regulated system of partition among solvents, they raised the chlorophyll content to 70 per cent from the 8 to 16 per cent found in the original extract, completing the separation by utilising the insolubility of chlorophyll in petroleum ether. By such means, 1 kilogrm. of dried stinging-nettles gave 6·5 grms. of the purified material, representing about 80 per cent of the total amount which the leaf contains, and application of the process to fresh leaves has established the identity of the product from both sources. Thus the isolation of chlorophyll from plants is now no more difficult than that of alkaloids or of sugars, and may actually be demonstrated as a lecture-experiment.

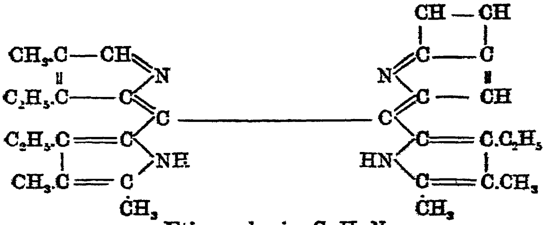
As a consequence of these operations, the dual nature of leaf-green was brought to light in 1912. The focus of main phytochemical action is thus revealed as a system composed of chlorophyll-*a*, bluish-green in solution, and of the yellowish-green chlorophyll-*b*, representing different stages of oxidation as indicated by the formulæ,

(*a*) $C_{32}H_{30}ON_4Mg(CO_2.CH_3)\ (CO_2.C_{20}H_{39}) = C_{55}H_{72}O_5N_4Mg$

(*b*) $C_{32}H_{28}O_2N_4Mg(CO_2.CH_3)\ (CO_2.C_{20}H_{39}) = C_{55}H_{70}O_6N_4Mg$

In the solid form these products are microcrsytalline powders, bluish-black and greenish-black respectively. They are accompanied by two non-nitrogenous yellow pigments, the unsaturated hydrocarbon, carrotene, $C_{40}H_{56}$, and its oxide, xanthophyll, $C_{40}H_{56}O$, both of which readily absorb oxygen and are allied to a third carrotinoid substance, fucoxanthin, $C_{40}H_{56}O_6$, associated with them in brown algæ and isolated in 1914. Based upon the experience indicated above, Willstätter and his colleagues have examined upwards of 200 plants drawn from numerous classes of cryptogams and phanerogams. The leaf-green of these is identical, and the proportion of *a* to *b* almost invariably approaches 3 : 1 excepting in the brown algæ, in which *b* is scarcely recognisable.

This is not an occasion to follow, otherwise than in the barest outline, the course of laboratory disintegration to which the chlorophyll molecules have been subjected by the controlled attack of alkalis and acids. The former agents reveal chlorophyll in the twofold character of a lactam and a dicarboxylic ester of methyl alcohol and phytol, an unsaturated primary alcohol, $C_{20}H_{39}.OH$, of which the constitution remains obscure in spite of detailed investigation of its derivatives; but the residual complex, representing two-thirds of the original molecule, has been carefully dissected. The various forms of this residual complex, when produced by the action of alkalis on chlorophyll, have been called "phyllins"; they are carboxylic acids of nitrogenous ring-systems, which retain magnesium in direct combination with nitrogen. The porphyrins are the corresponding products arising by the action of acids; they are carboxylic acids of the same nitrogenous ring-systems from which the magnesium has been removed. The phyllins and the porphyrins have alike been degraded to the crystalline base, ætioporphyrin, $C_{31}H_{36}N_4$, into the composition of which four variously substituted pyrrole rings enter, probably as follows:



Ætioporphyrin, $C_{31}H_{36}N_4$.

It is this assemblage of substituted pyrroles which, according to present knowledge, is the basic principle also of the blood-pigment, in which iron plays the part of magnesium in chlorophyll. Fundamental as is the difference between hæmoglobin and chlorophyll, relationship can be claimed through this connecting-link, because the same compound, ætioporphyrin has been produced from hæmoporphyrin, $C_{33}H_{36}O_4N_4$, which is thus its dicarboxylic acid. Hæmoporphyrin arises from hæmatoporphyrin, $C_{33}H_{38}O_6.N_4$, produced by the action of hydrobromic acid on hæmin, $C_{33}H_{32}O_4N_4FeCl$, which in turn is derived by exchanging chlorine for hydroxyl in hæmatin, $C_{33}H_{33}O_5N_4Fe$, the non-albuminoid partner of globin in hæmoglobin. Thus, omitting many intermediate stages, the relationship between chlorophyll and hæmoglobin may be sketched by the diagram (see Fig. 3).

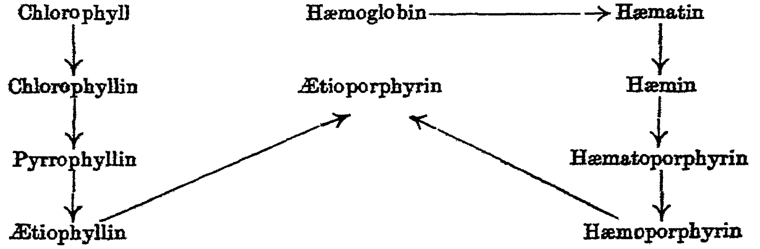



FIG. 3.

It must be remembered, however, that although recent years have witnessed great progress in elucidating the nature of chlorophyll and hæmoglobin, the mechanism by which they act remains unrevealed. The famous assimiliation hypothesis of von Baeyer, according to which it is formaldehyde which represents the connecting link in the phytochemical synthesis of carbohydrate from carbon dioxide, was enunciated in 1870, and arose from Butlerow's preparation of methylenitan. In spite of numerous criticisms, some of which are quite recent, it remains unshaken. The line of such criticism has taken two directions. Of the one hand, H. A. Spoehr (1913), from experiments suggested by the fact that the morning acidity of plant juices diminshes or disappears on exposure to light, has shown that this change is photochemical only, and may be independent of enzymes, the volatile products including formaldehyde. Emil Baur (1908, 1910, and 1913) has urged the claims of oxalic acid to be regarded as the first product of assimilation, and shows how this may lead to the other plant-acids, glycollic, malic, and citric, the first-named being a possible stepping-stone to the carbohydrates by resolution into formaldehyde (and formic acid), incidentally assuming towards malic and citric acids the relationship which glucose bears to starch. On the other hand, K. A. Hofmann and Schumpelt (1916) preceded by Bredig (1914), have attacked the hypothesis on the ground of kinetics, and imagine an electrolytic resolution of water under the influence of light, which liberates oxygen and effects the reduction of carbon dioxide by hydrogen to formaldehyde through formic acid.

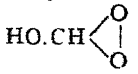
All these arguments have been weighed by Willstätter and Stoll (1917), who dismiss them on comparing the volume of carbon dioxide absorbed by leaves with the correspond-

ing volume of oxygen liberated. They point out that this assimilatory quotient, $CO_2/O_2$, which should be unity in the case of formaldehyde, becomes 1·33, 2 and 4 in the case of glycollic, formic, and oxalic acids respectively. Proceeding to determine this quotient experimentally, they found it to be unity, whether the temperature is 10° of 35°, whether the atmosphere is rich in carbon dioxide or free from oxygen, and alike with ordinary foliage or cactus. Furthermore, they found (1917) that whilst organic liquids holding chlorophyll in solution do not absorb more carbon dioxide than the liquids themselves, this gas is absorbed much more freely by chlorophyll hydrosols than by other colloidal solutions, a maximum assimilation of two molecular proportions to one magnesium atom being reached, when phæophytin is precipitated :—

$$C_{55}H_{72}O_5N_4Mg + 2CO_2 + 2H_2O = C_{55}H_{74}O_5N_4 + Mg(HCO_3)_2.$$

Prior to this change, which is the first stage appearing in a controlled disruption of chlorophyll-*a* by mineral acids, there is produced an intermediate compound resembling a hydrogen carbonate in which the metal retains a partial grip on the nitrogen (see Fig 4).

It is suggested that leaf-green unites with carbon dioxide by similar mechanism, and that the action of light on the above compound transforms the carbonic acid into an isomeride having the nature of a peroxide such as per-formic acid, H CO.O.OH, or formaldehyde peroxide,



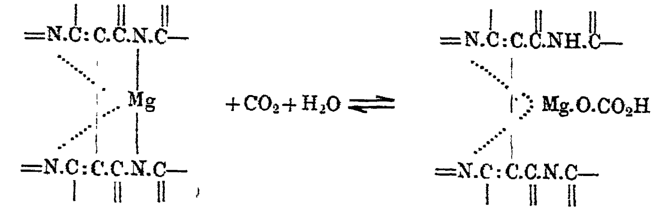


FIG. 4.

### *Anthocyans, the Pigments of Blossoms and Fruits.*

Since the days of Eden, gardens have maintained and extended their silent appeal to the more gentle emotions of mankind. The subject possesses a literature, technical, philosophical, and romantic, at least as voluminous as that surrounding any other industrial art, and the ambition to cultivate a patch of soil has attracted untold millions of human beings. Amongst manual workers none maintain a standard of orderly procedure and patient industry higher than that of the gardener. Kew and La Mortola defy the power of word-painters to condense their soothing beauty into adequate language, whilst that wonderful triangle of cultivation which has its apex at Grasse almost might be described as industry with a halo.

To the countless host of flower-lovers, however, it is probable that Grasse is the only connecting-link between chemistry and their cherished blossoms, they being dimly aware that the ingredients of some natural perfumes have been imitated in the laboratory. The circumstance that identical products of change are generated by the plant, however, and form but one section of the numberless chemical elaborations which proceed before their eyes escapes them because it has been ordained that chemistry is to occupy a backwater in the flood of knowledge Let us hope that before another century has passed this additional charm to the solace of a garden may be made more generally accessible.

Even to chemists it is only during the last decade that the mechanism of blossom-chemistry has been revealed. The subject has indeed excited their attention since an early period in the history of the organic branch, and the existing class name for blossom-pigments was first used by Marquart in 1835 to distinguish blue colouring-matters occurring in flowers. It is also interesting to us to notice that in the following year Dr. Hope, who presided over the birth of the Chemistry Section at the Edinburgh meeing in 1834, described experiments conducted with blossoms representing many different orders, and devised a classification of the pigments which they contain. The recognition of glucosides amongst the anthocyans appears to have been first made as recently as 1894, by Heise; about that period, also, it gradually became clear that the various colours assumed by flowers are not variations of a single substance common to all, but arise from a considerable number of non-nitrogenous pigments. Prior to 1913, the most fruitful attempt to isolate a colouring-matter from blossoms in quantity sufficient for detailed examination had been made by Grafe (1911), but the conclusions to which it led were inaccurate. In the year mentioned, however, Willstätter began to publish with numerous collaborators a series of investigations, extending over the next three years, which have brought the subject within the realm of systematic chemistry For the purpose of distinguishing glucosidic and non-glucosidic anthocyans the names anthocyanin and anthocyanidin respectively were applied. The experimental separation of anthocyanins from anthocyanidins was effected by partition between amyl alcohol and dilute mineral acid, the latter retaining the diglucosidic anthocyanins in the form of oxonium salts and leaving the anthocyanidins quantitatively in the amyl alcohol, from which they are not removed by further agitation with dilute acid; the monoglucosidic anthocyanins were found in both media, but left the amyl alcohol when offered fresh portions of dilute acid

(To be continued).

## THE ACTION OF AMMONIUM HYDRATE UPON MERCUROUS CHLORIDE.

By J. G. F. DRUCE, M Sc., A.I.C.

WHEN ammonium hydrate is added to insoluble mercurous chloride, the white solid is converted into "black precipitate" of the formula $NH_2Hg_2Cl$ The equation representing this reaction is usually given as:—

$$NH_4OH+Hg_2Cl_2=NH_2Hg_2Cl+H_2O+HCl.$$

This suggests that on mixing the reactants, one of which is neutral and the other is alkaline to indicators, the resultant products should react acid. Actually, it is found that this is not the case, and it was thought desirable to ascertain whether the hydrochloric acid represented as being formed was immediately neutralised by excess of ammonium hydrate.

This appears to be the correct view, since however little of the alkali is used, only one-half of it is accounted for by the above equation, which only represents an initial reaction. The hydrochloric acid produced is only momentarily free; it is immediately neutralised by a second equivalent of ammonium hydrate.

Quantitative experiments have been carried out to elucidate the nature of the reaction as follows. Mercurous chloride (0·942 grm.) was placed in a conical flask of 200 cc. capacity, and shaken with 10 cc. of water. 20 cc. of a normal solution of ammonium hydrate were added, and the whole was shaken, after inserting a stopper, and allowed to stand for 15 hours. The mixture still evolved the odour of ammonia, and was quickly filtered into a graduated flask (200 cc.), and the precipitate was washed several times with water. The volume of filtrate and washings was made up to 200 cc. 20 cc. were withdrawn and titrated against a decinormal solution of hydrochloric acid. This was repeated twice. The 20 cc. of filtrate required:—

| Expt. | cc. $\frac{N}{10}$ HCl |
|---|---|
| 1 | 8·00 |
| 2 | 7·90 |
| 3 | 7·95 |
| Mean | 7·95 |

Thus the free ammonium hydrate in the total filtrate was 0·556 grm. The quantity actually taken was 0·700 grm., therefore 0·144 grm. was used in the course of the reaction. The amount of soluble chloride ions formed was estimated as follows:—

20 cc. of the filtrate made up to 200 cc. were withdrawn and boiled for 15 minutes to drive off all free ammonia. The residual solution was then titrated with a fiftieth normal solution of silver nitrate, using potassium chromate as indicator. This was also repeated twice, and the following results were obtained.

| Expt. | cc. $\frac{N}{50}$ $AgNO_3$ |
|---|---|
| 1 | 9·20 |
| 2 | 9·15 |
| 3 | 9·10 |
| Mean | 9·15 |

Thus there was 0·098 grm of ammonium chloride in the whole solution.

These results are accurately expressed by the equation:—

$$2NH_4OH+Hg_2Cl_2=NH_2Hg_2Cl+NH_4Cl+H_2O$$

which requires that for 0·942 grm. of mercurous chloride, 0·140 grm. of ammonium hydrate should be used and 0·107 grm. of ammonium chloride should be obtained.

A difference of opinion exists regarding the nature of the black precipitate $NH_2Hg_2Cl$. Some chemists consider it to be a mixture of white precipitate, $NH_2HgCl$ and metallic mercury. If it is rubbed on to copper it does not amalgamate or perceptibly affect this metal. This is hardly to be expected if free mercury were present. Hence it seems more correct to regard the subtsance as a compound and not a mixture.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences.* Vol. clxxiii., No. 7.

"Influence of Temperature on the Viscosity of Normal Liquids."—By M. Edm. van Aubel.

"Dimensions of the Molecules of some Fatty Oils, and on some Phenomena of Molecular Solutions."—By. M. Paul Woog.

No 8.

"Depolarisation of Light by Liquids Holding in Suspension Crystalline Particles."—By M. St. Procopin.

No. 9

"Newton's Law and Einstein's Formula for the Perihelion of Planets."—By M. Gaston Bertrand.

## NOTES.

THE Registrar of the Institute of Chemistry has directed attention to an erroneous statement in Part IV. of the *Journal* of the Institute, to the effect that Dr. P. C. C. Isherwood had been appointed to a Lectureship in the University of Cambridge. Dr. Eric K. Rideal is Humphrey Owen Jones Lecturer in Physical Chemistry, and Dr. P. C. C. Isherwood is a Director of Messrs. W. J. Bush & Co. Ltd.

A SCHEME is afloat for "fertilising the air" to encourage plant growth. Experiments have been described by Dr. Gradenwitz, of New York. Various plants and vegetables were grown in an atmosphere artificially enriched with carbonic acid, and it is stated that an increased yield was obtained of spinach 150 per cent, potatoes 180 per cent, lupines 174 per cent, parsley 100 per cent.

Much interesting work is said to have been done, and further particulars may be obtained from Messrs. Wiskemann Smith & Co. Ltd., London, E.C.2.

Messrs. Siemens Bros. & Co. have equipped an extensive factory for the production of ebonite. From an advance proof of a new catalogue which we have just received, it is evident that the firm are manufacturing ebonite in all the forms used in the arts, both in the rough as tube, sheet, and block, and also in innumerable forms as finished articles, from high tension insulators to the mouthpieces of pipes. They are also introducing a new high-class insulating material under the name of "Keramot," which, judging from the claims made as its properties, is likely to find an extensive use in the electrical world.

The Polytechnic, Regent Street, London.—A course in Electrical Engineering has been arranged for the coming Session under the direction of Mr. Philip Kemp, M.Sc., Tech.M.I.E.E., and a competent staff. The courses, including Electrical engineering and subsidiary subjects, are arranged in various grades, and students are strongly recommended to avail themselves of these. In the first two years a student spends one evening per week in the Electrical Engineering Department, and two evenings per week in the succeeding years. At the close of the session examinations will be held in all stages, and students are expected to pass these examinations before proceeding to a more advanced class in the following year. Laboratory and home work are taken into consideration in determining a student's position. A silver medal may be awarded to the best student in the department, and bronze medals may be awarded to the best student in each year. Diplomas are awarded to students who have satisfactorily passed through the complete five year's course (including subsidiary subjects). Students are also prepared for the Final C. and G and A.M.I.E.E. Examinations. The Electrical Laboratory is well equipped with various types of modern machinery and apparatus. The plant includes D.C. motors and generators, alternators, A.C. motors of the synchronous, induction, and single-phase commutator types, rotary converters, transformers, and mercury arc rectifier—totalling about 50 machines. A wireless aerial is erected upon the roof of the building. The department possesses an Electrical Library which is available for the use of students during laboratory classes.

Institute of Brewing.—The Research Committee of this Institute (Brewers Hall, Addle Street, London, E.C.2) are carrying out a series of investigations on hop growing and preparation. Recently an invitation was given to a number of the more prominent hop growers to visit the Research Station and the Gardens of Messrs. Whitbread, and a profitable day was spent in examining the progress of the investigations. Messrs. Whitbread & Co. are erecting experimental kilns for systematic work on drying and preparation. Experiments are in progress with a view to studying the effect of varying temperatures with constant air current; variation air current with constant temperature; the influence of the moisture content of the hops; the effect of burning varying amounts of sulphur; the effect of products of combustion of open fires, etc. The Secretary of the Institute is Mr. W. H. Bird, who will give any further information on the subject.

Argentina State Railway Requirements.—A telegram from the Commercial Secretary to His Majesty's Legation at Buenos Aires states that the State Railways are inviting tenders for one year's supply of he following: chemicals (close October 17); paints and varnishes (close October 18); foundry materials (close October 19th); metals (close October 20th); electrical stores (close October 21); glass (close October 24). Tenders must be presented through a local agent, but it will be preferable to quote local merchants. A copy of the relative specifications cannot be expected in the Department of Overseas Trade before the arrival of the ordinary mail at the end of September.

Calcutta Motor Show.—H.M. Trade Commissioner reports that, by the decision of the Motor Traders' Association, the Calcutta Motor Show (to be held from December 19 to 24) will be open to all except ex-enemy countries.

Lemberg Fair.—With reference to the Lemberg Fair, preliminary notice of which was published in the *Journal* of July 7, the Department of Overseas Trade is informed that the dates for the Fair have been fixed for September 25 to October 5. The classes of exhibits include machinery, iron work, technical supplies, oil industry, metallurgy, textiles, agricultural and agricultural implements, transport, furniture, building material, hides and leather goods, china, &c., paper, photography, sports goods, chemical goods, lighting apparatus, food products, musical instruments, and propaganda. Enquiries regarding space, &c., should be addressed to Targi Wschodnie (Eastern Fairs and Market, Ltd.), Lwow, Poland.

An Exhibition Afloat.—According to present plans, a specially designed Exhibition Ship, under the title of *British Industry*, will set sail from the Thames in the summer of 1923, for the chief ports of the world. A company called the British Trade Ship, Ltd., has been formed, with registered offices at 12, Grosvenor Gardens, S.W.1, and a strong board assembled under the chairmanship of Earl Grey. Among the directors are the Vice-Chairman, Sir G. B. Hunter (Chairman of Messrs. Swan, Hunter & Co.), the Duke of Northumberland, Commdr. R. W. Day, Major G. P. Denton, Sir Maxwell Hicks, Messrs. J. W. Beaumont Pease, Noel E. Peck, T. E. Thirlaway, and Edmund Hill (General Secretary of the Federation of British Industries): The venture is likely to be of the greatest possible benefit to the export trade of the British Empire, and is bound to make a strong appeal to our merchants and manufaturers. This British Trade Ship will be specially constructed for the purposes of an exhibition, and every detail of her equipment, from the engines to the fittings and furniture, will itself be an exhibit of British workmanship at its best. She will be as large as a first-class liner, having a gross tonnage of 20,000 tons, and in her internal arrangements will differ from any ship that has ever been floated. The scheme of the Trade Ship

is a great advance on the old-time bagman proceeding from town to town, and packing and re-packing his meagre samples at each halting place. A comparison between the two methods will reveal an enormous saving of time and cost. The arrival at each trade centre of the great white ship *British Industry* will be an event long looked forward to. At each port Reception Committees will have been formed in advance, whose duties it will be to make known the advent of the sea-borne Exhibition, to prepare lists of important firms and individuals, the description of the business in which they are interested, and all other information which may be useful. Fuller details concerning the Floating Exhibition are, we understand, to be available at the Shipbuilding, Engineering, and Machinery Exhibition at Olympia, which opened on September 7.

FOREIGN EXHIBITORS AT THE UTRECHT FAIR.—Great Britain—as may be seen from the figures quoted below—stands high in point of numbers in the list of foreign nations exhibiting at the Utrecht Fair, being placed second only to Germany, and having more than twice as many exhibitors as France. A few more applications for space have been received since these figures were compiled, so that the final numbers will be slightly greater, but the relative proportion between the different countries will probably remain as it is. It will be seen that there are rather more than half as many foreign as Dutch stall-holders.

| | Direct Exhibitors. | Exhibiting through Dutch Agents. |
|---|---|---|
| Germany | 92 | 64 |
| England | 47 | 30 |
| Belgium | 31 | 12 |
| France | 21 | 10 |
| Switzerland | 8 | 13 |
| America | 4 | 11 |
| Czecho-Slovakia | 7 | 3 |
| Italy | 4 | 3 |
| Austria | 4 | 2 |
| Sweden | 2 | 1 |
| Finland | 2 | 0 |
| E. Africa | 1 | 0 |
| | 223 | 149 |
| Total Foreign Exhibitors | | 372 |
| Total Dutch Exhibitors | | 706 |
| Grand Total | | 1078 |

Two or three adverse factors have been encountered in securing the participation of the various European countries. The rate of exchange ruling with Holland makes exhibiting costs extremely high even for Belgium and France; while Austria, Italy, &c., are still more severely handicapped. An Austrian firm, for instance, has to pay 100,000 kronen for a space which costs a Dutch firm only 500 florins, and an English firm £45. The value of the £ sterling in Holland has changed so little that the price consideration is not such a serious one for the British exhibitor. The coal strike and the consequent disorganisation of business made it, however, absolutely impossible for many firms to participate who would otherwise have done so. The success or failure of the exhibition is naturally dependent upon the results obtained. So far as exhibits go, the Fair Authorities have certainly ensured a variety of products which should prove extremely attractive to the buyer who wishes to make a comprehensive and comparative survey of what post-war Europe is making.

TREATMENT OF PHOSPHATES BY CALCINATION WITH A VIEW TO THEIR EMPLOYMENT AS PHOSPHATIC FERTILISERS.—(1) Process (Wolter Phosphate).—At least 1200° C. 100 parts of phosphorite, 70 of acid soda sulphate, 20 of calcium carbonate; 22 of sand, and 6 to 7 of carbon are melted. The product when cooled is broken up, dessicated and pulverised. (2) Process (D.R.P. 240875).—Crude phosphate is melted at 2000° C. until a test piece when cooled, pulverised, and treated with diluted $SO_4H_2$ coagulates albumen. (3) Process (D R.P. 274409) (Phosphate Rhenania).—Phosphorites reduced to fragments are mixed with silico-potassic rocks, heated in special furnaces, without attaining melting point, until all hardens. (4) Process —Phosphatic substances are melted with a certain amount of lime and silica so as to obtain the combination $5CaO.P_2O_5SiO_2$. (5) Process.—Crude phosphates are heated with $CaCl_2$ or $MgCl_2$. The HCl liberated solubilises the phosphate. (6) Process (D.R.P. 258790).—Crude phosphate is melted with artificial silicates. The fused mass obtained is pulverised by aid of a current of steam. (7) Process.—Tetraphosphate (Italian invention) is obtained by calcination of finely pulverised phosphates with which 6 per cent alkalino-terreous carbonate is mixed. (8) Process.—The phosphoric acid of natural phosphates is made soluble in citrate by moderate heating with carbon, lime, wood, or petroleum. (9) Process (D.R.P. 715587).—Mixtures of phosphates of alumina are calcined at a temperature of at least 1150° C. with magnesia, in such proportion that a molecule of $P_2O_5$ will correspond to four molecules of MgO.—*Chimie et Industrie*, July, 1921.

SYNTHETIC ACETIC ACID.—The manufacture of acetic acid from acetylene, first accomplished by Berthelot, was yet in its infancy in 1914, but the effect of the war was to bring it within the field of industrial work. A history of this question and an account of the various difficulties encountered in the employment of scientific methods are given by M. Deschiens in *Chimie et Industrie* of March, April, and May. In conclusion, after mentioning the maximum normal productions of some synthetic acetic acid works, comparatively with those of acetic acid and lime acetate from pyroligneous systems, utilised in France and the United States, M. Deschiens remarks that the cost price of synthetic acid being now less, competition may be expected. However, some new applications are likely to absorb a production which will continue to increase, such as those in the cellulose acetate industry; synthetic indigo, and manufacture of various pharmaceutic products. In spite of this increase, competition, no doubt, will come into play. In his report on carbonising wood, M. Deschiens remarks that synthetic acetic acid, almost unlimited in production, will find its utilisation subordinate to cost price. It seems probable that new works for manufacture of a more or less great quantity of synthetic acetic acid will themselves utilise it and put acetic by-products in the markets, a procedure which cannot fail to result in a crisis of prices.—*Génie Civil*, July 9, 1921.

## NEW COMPANIES.

The under-mentioned particulars of New Companies recently registered are taken from the Daily Register compiled by JORDAN & SONS, LIMITED, Company Registration Agents, Chancery Lane, W.C 2.

COURTIN AND WARNER, LIMITED.—(176508)—Registered August 29th, 1921. 8, Harp Lane, E C. To carry on the business of Manufacturing Chemists Nominal Capital: £20,000 in 20,000 Ordinary Shares of £1 each. Directors: H. G. Warner, 28, Homefield Road, Wimbledon Common, S W, L E Courtin, Sill Lodge, Stonebridge Park, N.W.10. Qualification of Directors: 50 Shares.

BURNS (WESTHOUGHTON), LIMITED.—(176505)—Registered August 29th, 1921. Railway Works, Slack Lane, Westhoughton, Lancashire To carry on the business of Wholesale and Retail and Manufacturing Chemists Nominal Capital. £3,000 in 3,000 Shares of £1 each. Directors· Catherine Holt, 192, Chorley New Road, Bolton; J. Lythgoe. 31, Park Aveuue, Sharples Park, Bolton; E. Cutsforth, 69, Swan Lane, Bolton. Qualification of Directors £100. Remuneration of Directors: 50% of the net half-yearly profits.

G. CLARKSON, LIMITED.—(176498)—Registered August 27th, 1921. 26, Wortley Lane, Leeds. To acquire and carry on the business of Pharmacy and Drug Store Proprietors Nominal Capital: £200 in 200 Shares of £1 each Directors: G. Clarkson, 10, Alcester Road, Leeds; Florence Clarkson, 10, Alcester Road, Leeds; F. Lockwood, 25, Station Road, Golcar, Near Huddersfield Qualification of Directors 1 Share. Remuneration of Directors: To be voted by Company.

RAINBOW DYES, LIMITED.—(176517)—Registered August 29th, 1921. To carry on the business of Dyers. Nominal Capital: £2,000 in 1,900 Shares of £1 each and 2,000 Shares of 1/- each. Directors: To be appointed by Subscribers. Remuneration of Directors· To be voted by Company in General Meeting. Subscribers: J. E. Stevens, 27, Trigon Road, Clapham, S W.; R. Martin, Hawthorn Cottage, York Square, Stepney, E.14.

A. E. ASHBY, LIMITED.—(176523)—Registered August 30th, 1921. 105, Woodhouse Street, Leeds. To carry on the business of Chemists and Druggists. Nominal Capital: £500 in 500 Shares of £1 each. Directors· A E. Ashby, 105, Woodhouse Street, Leeds; Alice Ashby, 105, Woodhouse Street Leeds. Qualification of Directors: 1 Share. Remuneration of Directors: To be voted by Company in General Meeting.

## New Patents.

THIS List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

22436—Davies, J.—Laying of magnesium cements on metallic surfaces. August 24.
22381—General Electric Co., Ltd.—Manufacture of tungsten. August 23.
22645—Hansford, J. B.—Manufacture of neutral sulphate of ammonia August 26.
22270—Hoover Co.—Process of recovering aluminium chloride from spent or partly-spent catalyzing agent. August 22.
22281—Macullam, A D.—Derivatives of nitrophenylstibinic acid, and process of preparing same. August 22.
22393—Soc. l'Air Liquide Soc Anon. pour l'Étude et l'Exploitation des procedes, G Claude.—Synthesis of ammonia. August 23.

*Specification published this Week.*

167941—British Cellulose and Chemical Manufacturing Co., Ltd, Bader, W. and Nightingale, D. A.—Manufacture of alkylamides aromatic sulphonic acids.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.



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THE CHEMICAL NEWS.
VOL. CXXIII., No. 3206.

# BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

EDINBURGH, 1921.

## THE LABORATORY OF THE LIVING ORGANISM.

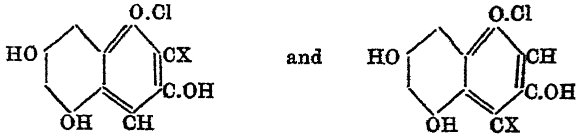
ADDRESS DELIVERED BEFORE SECTION B (CHEMISTRY)

BY M. O. FORSTER, D.Sc., F.R.S., President of the Section.

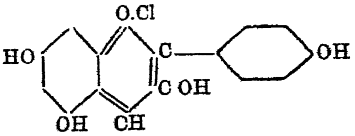
(Concluded from p. 152).

THE earliest of these papers, published in conjunction with A. E. Everest, dealt with cornflower pigments, and indicated that the distinct shades of colour presented by different parts of the flower are caused by various derivatives of one substance; thus the blue form is the potassium derivative of a violet compound which is convertible into the red form by oxonium salt-formation with a mineral or plant acid. Moreover, as found in blossoms, the chromogen was observed to be combined with two molecular proportions of glucose and was isolated as crystalline cyanin chloride; hydrolysis removed the sugar and gave cyanidin chloride, also crystalline. Applying these methods more generally, Willstätter and his other collaborators have examined the chromogens which decorate the petals of rose, larkspur, hollyhock, geranium, salvia, chrysanthemum, gladiolus, ribes, tulip, zinnia, pansy, petunia, poppy, and aster, whilst the fruitskins of whortleberry, bilberry, cranberry, and cherry, plum grape, and sloe, have also been made to yield the pigment to which there characteristic appearance is due.

The type of structural formula by which the anthocyanidins are now represented was proposed in 1914, simultaneously and independently by Willstätter and by Everest; incidentally their separate memoirs afford an unusual example of synchronous publication, each having been communicated to the respective academies on the same day, March 26. Willstätter identified phloroglucinol (1:3 : 5-trihydroxybenzene) as a common product of hydrolysing anthocyanidins with alkali, obtaining also *p*-hydroxybenzoic acid from pelargonidin, protocatechuic (3 : 4-dihydroxybenzoic) acid from cyanidin, and gallic (3 : 4 : 5-trihydroxybenzoic) acid from delphinidin. Accordingly he suggested for the anthocyanidin chlorides two alternative formulæ



in which X represents the substituted benzene ring which appears in the form of a phenolcarboxylic acid on hydrolysis. Later in the same year he confirmed (with Mallison) the former of these representations by reducing quercitin to cyanidin chloride (see Fig. 5) and (with Zechmeister) by effecting a complete synthesis of pelargonidin chloride



from 2 : 4 : 6-trihydroxybenzaldehyde.

Everest reached the same conclusion by recognising the significance of the fact that a flavone, *e.g.*, luteolin, and a flavonol, *e.g.*, morin, yield red pigments on reduction; he therefore reduced quercitrin (the rhamnoside of quercitin) to cyanidin, and rutin (the rhamnoglucoside of quercitin, and identical with osyritin, myrticolorin, and violaquercitrin) to cyanin. Moreover, he showed that the petals of many yellow flowers, *e.g.*, daffodil, wallflower, tulip, crocus, jasmin, primrose, and viola, or the white blossoms of narcissus, primula, and tulip all yield red pigments on careful reduction, and in subsequent papers (*e.g.*, with A. J. Hall, 1921) has indicated reduction of yellow sap-pigments belonging to the flavonol group as representing the probable course of anthocyan-formation in plants. In this connection it is noteworthy that an association between the pigments of sap and of blossoms was adumbrated in 1855 by Martens, who suggested that a faintly yellow substance in plant sap, when oxidised in presence of alkalis and light, produces the yellow pigments, and that these, by further oxidation, change into the red colouring-matters. Everest has shown that reduction is the process actually involved and that flavonols are the precursors of anthocyans, not *vice versa* as suggested by other investigators; moreover, he found (1918) that "Black Knight" petals contain a glucoside of delphinidin, whilst the corresponding flavonol, myricetin, is present in the sap, also as a glucoside (see Fig. 6).

Hence it will be seen that pelargonidin, cyanidin, delphinidin, corresponding to the three abovementioned phenolcarboxylic acids, are the fundamental materials in the group of anthocyan pigments, and that they are derived from the three

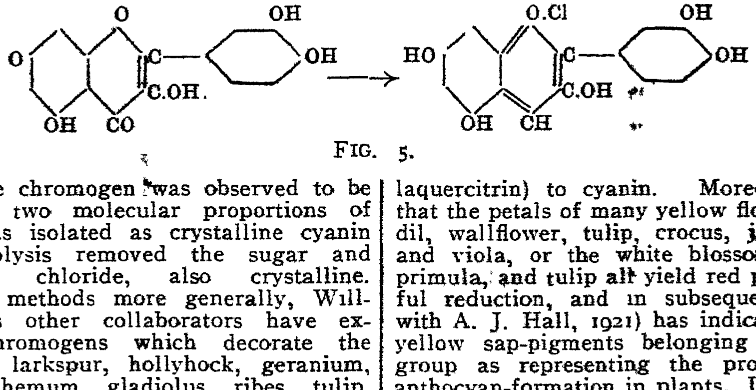
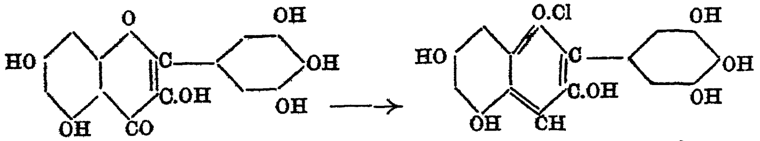


FIG. 5.

flavonols, kaempferol, quercitin, and myricetin respectively. The variations upon these types which present themselves in blossoms are twofold, due to (1) the number and position of entrant methyl groups, and (2) the number and character of the aldose molecules which go to form their glucosides. Belonging to the first group are peonidin (monomethylated cyanidin), ampelopsidin, myrtillidin, and petunidin (monomethylated delphinidin) with malvidin and oenidin (dimethylated delphinidin). The second group arise from combination with glucose, galactose, or rhamnose, the greatest proportion of pigments occurring as mono- or diglucosides. Thus callistephin and salvinin are the mono- and diglucoside of pelargonidin; asterin and chrysanthemin are monoglucosides and idaein a galactoside of cyanidin, derived from which are the diglucosides cyanin and mekocyanin, and the rhamnoglucoside, keracyanin; violanin is a rhamnoglucoside of delphinidin, whilst delphinin, when hydrolysed with hydrochloric acid, yields delphinidin chloride, glucose, and *p*-hydroxybenzoic acid in the molecular proportion, 1 · 2.

Thus may the chemist find fresh delight in the hedgerow and the garden by reflecting on the processes which lead to the molecular structures lying well within his mental horizon, and adorning those familiar models with all the chromatic splendours of snapdragon, pansy, rose, and larkspur. The gustatory and æsthetic thrill engendered in consuming summer pudding and custard is heightened by the soothing blend of egg-yolk lutein and the crimson contributed to the colour scheme by the raspberry and currant anthocyanins.



Myricetin. Delphinidin Chloride.

Fig. 6.

### *Micro-Biochemistry.*

Amongst the many sources of pleasure to be found in contemplating the wonders of the universe, and denied to those untrained in scientific principles, is an appreciation of infra-minute quantities of matter. It may be urged by some that within the limits of vision imposed by telescope and microscope, ample material exists to satisfy the curiosity of all reasonable people, but the appetite of scientific inquiry is insatiable, and chemistry alone, organic, inorganic, and physical, offers an instrument by which the investigation of basal changes may be carried to regions beyond those encompassed by the astronomer and the microscopist.

It is not within the purpose of this address to survey that revolution which is now taking place in the conception of atomic structure; contributions to this question will be made in our later proceedings and will be followed with deep interest by all members of the Section. Fortunately for our mental balance, the discoveries of the current century, whilst profoundly modifying the atomic imagery inherited from our predecessors, have not yet seriously disturbed the principles underlying systematic organic chemistry; but they emphasise in a forcible manner the intimate connection between different branches of science, because it is from the mathematical physicist that these new ideas have sprung. Their immediate value is to reaffirm the outstanding importance of borderline research and to stimulate interest in submicroscopic matter.

This interest presents itself to the chemist very early in life and dominates his operations with such insistence as to become axiomatic. So much so that he regards the universe as a vast theatre in which atomic and molecular units assemble and interplay, the resulting patterns into which they fall depending on the physical conditions imposed by nature. This enables him to regard micro-organisms as co-practitioners of his craft, and the chemical achievements of these humble agents have continued to excite his admiration since they were revealed by Pasteur. The sixty years which have now elapsed are rich in contributions to that knowledge which comprises the science of micro-biochemistry, and in this province, as in so many others, we have to deplore the fact that the principal advances have been made in countries other than our own. On this ground, fortified by the intimate relation of the science to a number of important industries, A. Chaston Chapman, in a series of illuminating and attractive Cantor Lectures in December, 1920, iterated his plea of the previous year for the foundation of a National Institute of Industrial Micro-biology, whilst H. E. Armstrong, in Birmingham a few weeks later, addressed an appeal to the brewing industry, which, although taking the form of a memorial lecture, is endowed with many lively features depicting in characteristic form the manner in which the problems of brewing chemistry should, in his opinion, be attacked.

Lamenting as we now do so bitterly the accompaniments and consequences of war, it is but natural to snatch at the slender compensations which it offers, and not the least among these must be recognised the stimulus which it gives to scientific inquiry. Pasteurs *Etudes sur la Bière* were inspired by the misfortunes which overtook his country in 1870-71, and the now well-known process of Connstein and Lüdecke for augmenting the production of glycerol from glucose was engendered by parallel circumstances. That acquaintance with the yeast-cell which was an outcome of the former event had, by the time of the latter discovery, ripened into a firm friendship, and those who slander the chemical activities of this genial fungus are defaming a potential benefactor. Equally culpable are those who ignore them. If children were encouraged to cherish the same intelligent sympathy with yeast-cells which they so willingly display towards domestic animals and silkworms, perhaps there would be fewer crazy dervishes to deny us the moderate use of honest malt-liquors and unsophisticated wines, fewer pitiable maniacs to complicate our social

problems by habitual excess.

Exactly how the cell accomplishes its great adventure remains a puzzle, but many parts of the machinery have already been recognised. Proceeding from the discovery of zymase (1897), with passing reference to the support thus given by Buchner to Liebig's view of fermentation, Chapman emphasises the importance of contributions to the subject by Harden and W. J. Young, first revealing the dual nature of zymase and the distinctive properties of its co-enzyme (1904), next in recognising the acceleration and total increase in fermentation produced by phosphates, consequent on the formation of a hexose-diphosphate (1908):

$$2C_6H_{12}O_6+2Na_2HPO_4= 2CO_2+2C_2H_6O+C_6H_{10}O_4(PO_4Na_2)_2+2H_2O.$$

In this connection it will be remembered that a pentose-phosphate is common to the four nucleotides from which yeast nucleic acid is elaborated. The stimulating effect developed by phosphates would not be operative if the cell were not provided with an instrument for hydrolysing the hexose-diphosphate as produced, and this is believed by Harden to be supplied in the form of an enzyme, hexosephosphatase, the operation of which completes a cycle. As to the stages of disruption which precede the appearance of alcohol and carbon dioxide, that marked by pyruvic acid is the one which is now most favoured. The transformation of pyruvic acid into acetaldehyde and carbon dioxide under the influence of a carboxylase, followed by the hydrogenation of aldehyde to alcohol, is a more acceptable course than any alternative based upon lactic acid. Moreover, Fernbach and Schoen (1920) have confirmed their previous demonstration (1914) of pyruvic acid formation by yeast during alcoholic fermentation.

The strict definition of chemical tasks allotted to yeasts, moulds, and bacteria suggests an elaborate system of microbial trades-unionism. E. C. Grey (1918) found that *Bacillus coli communis* will, in presence of calcium carbonate, completely ferment forty times its own weight of glucose in forty-eight hours, and later (1920) exhibited the threefold character of the changes involved which produce (1) lactic acid, (2) alcohol with acetic and succinic acids, (3) formic acid, carbon dioxide, and hydrogen. Still more recent extension of this inquiry by Grey and E. G. Young (1921) has shown that the course of such changes will depend on the previous experience of the microbe. When its immediate past history is anærobic, fermentation under anærobic conditions yields very little or no lactic acid, and greatly diminishes the production of succinic acid, whilst acetic acid appears in its place; admission of oxygen during fermentation increases the formation of lactic, acetic, and succinic acids, diminishes the formation of hydrogen, carbon dioxide, and formic acid, but leaves the quantity of alcohol unchanged. The well-known oxidising effect of *Aspergillus niger* has been shown by J. N. Currie (1917) to proceed in three stages marked by citric acid, oxalic acid, and carbon dioxide, whilst Wehmer (1918) has described the conditions under which citric acid and, pricpally, fumaric acid are produced by *Aspergillus fumaricus*, a mould also requiring oxygen for its purpose. The lactic bacteria are a numerous family and resemble those producing acetic acid in their venerable record o service to mankind, whilst among the most inter esting of the parvenus are those responsible fo the conversion of starch into butyl alcohol an acetone. Although preceded by Schardinge (1905), who discovered the ability of *B. maceran* to produce acetone with acetic and formic acids but does not appear to have pursued the matte further, the process associated with the name o A. Fernbach, and the various modifications whicl have been introduced during the past ten year are those best known in this country, primaril because of the anticipated connection with syn thetic rubber, and latterly on account of the ace tone famine arising from the War. The King's Lynn factory was resuscitated and arrangement had just been completed for adapting spirit dis tilleries to application of the process when, owing to the shortage of raw material in 1916, operation were transferred to Canada, and ultimately attained great success in the factory of British Acetones, Toronto.

Much illuminating material is to be found in the literature of 1919-20 dealing with this question in its technological and bacteriological aspects. Ingenuity has been displayed in attempting to explain the chemical mechanism of the process, the net result of which is to produce roughly twice as much butyl alcohol as acetone. The fermentation itself is preceded by saccharification of the starch, and in this respect the bacteria resemble those moulds which have lately been brought into the technical operation of starch-conversion, especially in France. The amyloclastic property of certain moulds has been known from very early times, but its application to spirit manufacture is of recent growth and underlies the amylo-process which substitutes *Mucor Boulard* for malt in effecting saccharification. Further improvement on this procedure is claimed for *B. mesentericus* which acts with great rapidity on grain which has been soaked in dilute alkali; it has the advantage of inferior proteolytic effect, thus diminishing the waste of nitrogenous matter in he raw material.

Reviewing all these circumstances we find that, just as the ranks of trades-union labour comprise every kind of handicraftsman, the practitioners of micro-biochemistry are divisible into producers of hydrogen, carbon dioxide, formic acid, acetaldehyde, ethyl alcohol, acetic, oxalic, and fumaric acids, acetone, dihydroxyacetone, glycerol pyruvic, lactic, succinic and citric acids, butyl alcohol, butyric acid. Exhibiting somewhat greater elasticity in respect of overlapping tasks, they nevertheless go on strike if underfed or dissatisfied with their conditons;; on the other hand, with sufficient nourishment and an agreeable temperature, these micro-trades-unionists display the unusual merit of working for 24 hours a day. One thing, however, they have consistently refused to do. Following his comparison of natural and synthetic monosaccharides towards different families of yeast (1894), Fischer and others have attempted to beguile unsuspecting microbes into acceptance of molecules which do not harmonise with their own enzymic asymmetry. Various *apéritifs* have been administered by skilled *chefs de cuisine*, but hitherto the little fellows have remained obdurate.

*Photosynthesis.*

Beyond a placid acceptance of the more obvious benefits of sunshine, the great majority of educated people have no real conception of the sun's contribution to their existence. What proportion of those who daily use the metropolitan system of tube-railways, for instance, could trace the connection between their progress and the sun? Very moderate instruction comprising the elements of chemistry and energy would enable most of us to apprehend this modern wonder, contemplation of which might help to alleviate the distresses and exasperation of the crush-hours.

For many years past, the problem connected with solar influence which has most intrigued the chemist is to unfold the mechanism enabling green plants to assimilate nitrogen and carbon. Although atmospheric nitrogen has long been recognised as the ultimate supply of that element from which phyto-protoplasm is constructed, modern investigation has indicated as necessary a stage involving association of combined nitrogen with the soil prior to absorption of nitrogen compounds by the roots, with or without bacterial cooperation. Concurrently, the agency by which green plants assimilate carbon is believed to be chlorophyll, operating under solar influence by some such mechanism as has been indicated in a preceding section.

Somewhat revolutionary views on these two points have lately been expressed by Benjamin Moore, and require the strictest examination, not merely owing to the fundamental importance of an accurate solution being reached, but also on account of the stimulating and engaging manner in which he presents the problem. Unusual psychological features have been introduced. Moore's "Biochemistry," published three months ago, will be read attentively by many chemists, but the clarity of presentation and the happy sense of conviction which pervade its pages must not be allowed to deter independent inquirers from confirming or modifying his conclusions. The book assumes a novel biochemical aspect by describing the life-history of a research. The first two chapters, written before the experiments were begun, suggest the conditions in which the birth of life may have occurred, whilst their successors describe experiments which were conducted as a test of the speculations and are already receiving critical attention from others (*e.g.*, Baly, Heilbron and Barker, *Transactions of the Chemical Society*, 1921, p. 1025).

It is with these experiments that we are, at the moment, most concerned. The earliest were directed towards the synthesis of simple organic materials by a transformation of light energy under the influence of inorganic colloids, and indicated that formaldehyde is produced when carbon dioxide passes into uranium or ferric hydroxide sols exposed to sunlight or the mercury arc lamp. Moore then declares that, although since the days of de Saussure (1804) chlorophyll has been regarded as the fundamental agent in the photosynthesis of living matter, there is no experimental evidence that the primary agent may not be contained in the colourless part of the chloroplast, chlorophyll thus being the result of a later synthetic stage. "The function of the chlorophyll may be a protective one to the chloroplast when exposed to light, it may be a light screen as has been suggested by Pringsheim, or it may be concerned in condensations and polymerisations subsequent to the first act of synthesis with production of formaldehyde" (p. 55). In this connection it is significant that chlorosis of green plants will follow a deficiency of iron even in presence of sunlight (Molisch, 1892), and that development of chlorophyll can be restored by supplying this deficiency, although iron is not a component of the chlorophyll molecule; moreover, green leaves etiolated by darkness and then exposed to light regain their chlorophyll, which is therefore itself a product arising from photosynthesis.

H. Thiele (1907) recorded the swift conversion of nitrate into nitrite by the rays from a mercury quartz lamp, whilst O. Baudisch (1910) observed that daylight effects the same change, and from allied observations was led (1911) to conclude that assimilation of nitrate and nitrite by green plants is a photochemical process. Moore found (1918) that in solutions of nitrate undergoing this reduction green leaves check the accumulation of nitrite, indicating their capacity to absorb the more active compound. Proceeding from the hypothesis that one of the organisms arising earliest in the course of evolution must have possessed, united in a single cell, the dual function of assimilating both carbon and nitrogen, he inquired (1918) whether the simplest unicellular algæ may not also have this power. He satisfied himself that in absence of all sources of nitrogen excepting atmospheric, and in presence of carbon dioxide, the unicellular algæ can fix nitrogen, grow and form proteins by transformation of light energy; the rate of growth is accelerated by the presence of nitrites or oxides of nitrogen, the latter being supplied in gaseous form by the atmosphere. From experiments (1919) with green seaweed (*Enteromorpha compressus*), Moore concluded also that marine algæ assimilate carbon from the bicarbonates of calcium and magnesium present in sea-water, which thereby increases in alkalinity, and further convinced himself that the only source of nitrogen available to such growth is the atmosphere. A description of these experiments, which were carried out in conjunction with E. Whitley and T. A. Webster, has appeared also in the *Proceeding of the Royal Society*, 1920 and 1921.

For the purpose of distinguishing between (1) the obsolete view of a vital force disconnected with such forms of energy as are exhibited by non-living transformers and (2) the existence in living cells of only such energy forms as are encountered in non-living systems, Moore uses the expression "biotic energy" to represent that form of energy peculiar to living matter. "The conception, in brief, is that biotic energy is just as closely, and no more, related to the various forms of energy existing apart from life, as these are to one another, and that in presence of the proper and adapted energy transformer, the living cell, it is capable of being formed from or converted into various of these other forms of energy, the law of conservation of energy being obeyed in the process just as it would be if an exchange were taking place between any two or more of the inorganic forms" (p. 128). The most characteristic feature of biotic energy, distinguishing it from all other forms, is the power which it confers upon the specialised transformer to proliferate.

*Conclusion.*

In "The Salvaging of Civilisation," H. G. Wells has lately directed the attention of thoughtful people to the imperative need of reconstructing our outlook on life. Convinced that the state-motive which, throughout history, has intensified the self-motive must be replaced by a world-motive if the whole fabric of civilisation is not to crumble in ruins, he endeavours to substitute for a League of Nations the conception of a World State. In the judgment of many quite benevolent critics his essay in abstract thought lacks practical value because it underestimates the combative selfishness of individuals. Try to disguise it as one may, this quality is the one which has enabled man to emerge from savagery, to build up that most wonderful system of colonial organisation, the Roman Empire, and to shake off the barbaric lethargy which engulfed Europe in the centuries following the fall of Rome. The real problem is how to harness this combative selfishness. To eradicate it seems impossible, and it has never been difficult to find glaring examples of its insistence among the apostles of eradication. Why cry for the moon? Is it not wiser to recognise this quality as an inherent human characteristic, and whether we brand it as a vice or applaud it as a virtue endeavour to bend it to the elevation of mankind? For it could so be bent. Nature ignored or misunderstood is the enemy of man: nature studied and controlled is his friend. If the attacking force of this combative selfishness could be directed, not towards the perpetuation of quarrels between different races of mankind, but against nature, a limitless field for patience, industry, ingenuity, imagination, scholarship, aggressiveness, rivalry, and acquisitiveness would present itself; a field in which the disappointment of baffled effort would not need to seek revenge in the destruction of our fellow-creatures; a field in which the profit from successful enterprise would automatically spread through all the communities. Surely it is the nature-motive, as distinct from the state-motive or the world-motive, which alone can salvage civilisation.

Before long, as history counts time, dire necessity will have impelled mankind to some such course. Already the straws are giving their proverbial indication. The demand for wheat by increasing populations, the rapidly diminishing supplies of timber, the wasteful ravages of insect pests, the less obvious, but more insidious depredations of our microscopic enemies, and the blood-curdling fact that a day must dawn when the last ton of coal and the last gallon of oil have been consumed, are all circumstances which, at present recognised by a small number of individuals comprising the scientific community, must inevitably thrust themselves upon mankind collectively. In the campaign which will then follow, chemistry must occupy a prominent place because it is this branch of science which deals with matter more intimately than any other, revealing its properties, its tranformations, its application to existing needs, and its response to new demands. Yet the majority of our people are denied the elements of chemistry in their training, and thus grow to manhood without the slightest real understanding of their bodily processes and composition, of the wizardry by which living things contribute to their nourishment and to their æsthetic enjoyment of life.

It should not be impossible to bring into the general scheme of secondary education a sufficiency of chemical, physical, mechanical, and biological principles to render every boy and girl of sixteen possessing average intelligence at least accessible by an explanation of modern discoveries. One fallacy of the present system is to assume that relative proficiency in the inorganic branch must be attained before approaching organic chemistry. From the standpoint of correlating scholastic knowledge with the common experiences and contacts of daily life this is quite illogical, from baby's milk to grandpapa's Glaxo the most important things are organic, excepting water. Food (meat, carbohydrate, fat), clothes (cotton, silk, linen, wool), and shelter (wood) are organic, and the symbols for carbon, hydrogen, oxygen, and nitrogen can be made the basis of skeleton representations of many fundamental things which happen to us in our daily lives without first explaining their position in the periodic table of all the elements. The curse of mankind is not labour, but waste; misdirection of time, of material, of opportunity, of humanity

Realisation of such an ideal would people the ordered communities with a public alive to the verities, as distinct from irrevelancies of life, and apprehensive of the ultimate danger with which civilisation is threatened. It would inoculate that public with a germ of the nature-motive, producing a condition which would reflect itself ultimately upon those entrusted with government. It would provide the mental and sympathetic background upon which the future truthseeker must work, long before he is implored by a terrified and despairing people to provide them with food and energy. Finally, it would give an unsuspected meaning and an unimagined grace to a hundred commonplace experiences. The quivering glint of massed bluebells in broken sunshine, the joyous radiance of young beech leaves against the stately cedar, the perfume of hawthorn in the twilight, the florid majesty of rhododendron, the fragrant simplicity of lilac, periodically gladden most careless heart and the least reverent spirit; but to the chemist they breathe an added message, the assurance that a new season of refreshment has dawned upon the world, and that those delicate syntheses, into the mystery of which it is his happy privilege to penetrate, once again are working their inimitable miracles in the laboratory of the living organism.

## THE TIME INTERVAL BETWEEN THE ABSORPTION AND EMISSION OF LIGHT IN CASES OF FLUORESCENCE.*

By PROF. R. W. WOOD, For.Mem.R.S.

IN the case of mercury vapour, illuminated by the instantaneous flash of an aluminium spark, it has been found that the vapour remains non-luminous during the period of excitation and for about 1/15000 sec. after, subsequently bursting out in a flash of green fluorescent light. This appears to

*Read before the British Association, Edinburgh Meeting (Section A).

be the first observation of a fluorescent or phosphorescent body remaining dark during the period of illumination. Other substances have been observed with a new type of phosphoroscope which records the phenomena of phosphorescence to 1/400000 sec. Nothing analogous in its behaviour to mercury vapour has been found up to the present time, however.

It is only freshly formed mercury vapour which exhibits the phenomenon of fluorescence. No trace of visible luminescence is shown by mercury vapour at any density, or by any light stimulation, *unless metallic mercury is present* and liberating nascent molecules. It is believed that these are diatomic when they first leave the metal, subsequently breaking up into monatomic molecules.

## APRICOT KERNEL OIL AND ITS CONGENERS.

### Possible Substitutes for Almond Oil.

By CHAS. F. JURITZ, M.A., D.Sc.,
Agricultural Research Chemist.

Some years ago a correspondent of *The Chemist and Druggist* complained of the confusion caused by the similarity of names assigned by the British Pharmacopœia and its adjuncts to the various oils derived from the almond, the apricot, and the peach. These names include :—

1. *Oleum amygdalae* or *Oleum amygdalae dulcis*: Almond oil, or oil of sweet almonds.
2. *Oleum amygdalae amarae essentiale*: Essential oil of bitter almonds.
3. *Oleum amygdalae persicae*: Peach kernel (or apricot kernel) oil.
4. *Oleum amygdalae persicae essentiale*: Essential oil of peach (or apricot) kernels.

Nos. 1 and 3 of the above are very similar to each other in character and constitution. They are both fixed oils: that is to say, they are not capable of being distilled but decompose on the continued application of heat. They pre-exist as fixed oils in the seeds of the almonds, the peach, and the apricot.

Nos. 2 and 4 also bear considerable resemblance to one another, but differ greatly from Nos. 1 and 3. They are both volatile essential oils, distilling readily at a conveniently low temperature. They do not occur naturally in apricot, peach, or almond kernels, but are formed only when these kernels are subjected to special treatment.

A short explanation may suffice to make the latter statement more clear. The kernels of the apricot and the peach, as well as *bitter* almonds, contain a nitrogenous bitter principle, or glucoside, called amygdalin. When acted on in a certain way by dilute acids or by natural ferments, this bitter principle is broken up, and the volatile oil above spoken of is formed. Now it so happens that apricot and peach kernels, as well as almonds, *both bitter and sweet*, contain a ferment known as emulsin, which consists of two enzymes prunase and amygdalase. This ferment is capable of acting on amygdalin, producing what we know as the essential oil of bitter almonds, the amygdalin in the process taking up water and forming benzaldehyde and hydrocyanic acid.

It follows then that from the seeds above referred to we can obtain these two classes of oil, first obtaining the fixed oil by what is called cold expression, and then allowing the ferment to act freely on the oil-freed residue so as to produce the essential oil which is subsequently obtained by the process of distillation.

Passing over from the general to the particular we may now take a very brief glance at each of these oils in turn.

*Almond Oil.*—Almond oil (*Oleum amygdalae*), as above stated, is a fixed oil. It is one of the non-drying class, and belongs to the olive oil group. It consists, when pure, mainly of olein, together with a little linolein and palmitin, but is free from stearin. It is almost water-white in colour and almost tasteless in flavour. The odour, too, is barely perceptible. It is obtained by cold expression from either the sweet or the bitter almond. Sweet almonds yield from 40 per cent to 45 per cent of this oil, and bitter almonds from 35 per cent to 38 per cent. It is usually prepared from bitter almonds, which are a cheaper source, especially as the residual cake after expression of the fixed oil can be used for the preparation of the essential oil.

According to Lewkowitsch the fixed oil so obtained does not easily turn rancid, as Allen says it does. Lewkowitsch also states that "oil of sweet Almonds, French," is nothing else but apricot kernel oil, or a mixture of the latter with peach kernel oil. These are so closely related to almond oil that distinction between the two is very closely related to almond oil that distinction between the two is very difficult. Almond oil is usually employed only in pharmacy, its high cost (4s. to 5s. per lb.) precluding its employment for other purposes. It has had, however, an extensive use medicinally as a demulcent, emollient, and laxative, serves well in cough-mixtures, and is said to be better adapted than olive oil for ointments and emulsions, producing a whiter ointment. It has, furthermore, found employment as a cosmetic and in soap manufacture. It is officially designated by the British Pharmacopœia as a constituent of certain liniments, oils, and ointments. The positon in South Africa, it is understood, is that even for pharmaceutical preparations true almond oil is seldom used (on account of its high price), except in cases where its employment is imperative. Accordingly pharmacists have been turning their attention to the substitution of other oils.

*Peach Kernel Oil.*—As already stated, apricot and peach kernel oils are very similar to almond oil in character, and can, in most cases, be substituted for the latter without detriment, and at less cost to the producer. They are obtained from apricot and peach kernels respectively by a process corresponding to that whereby almond oil is obtained from almonds. Peach kernels, thus treated, yield from 32 to 35 per cent of fixed oil. and its chief employment is as a substitute for almond oil. Bieber, in fact, asserted that most of the almond oil of commerce (*Oleum amygda-*

lae) is really only peach kernel oil (*Oleum amygdalae persicae*). Even the latter, however, is too high in price at 3s. per lb. to assure its general use, and hence, wherever possible, its place—in South Africa at least—has been taken mainly by pea-nut oil (*Oleum arachis*) for toilet articles and in other cases where the use of pea-nut or sesame oil is permissible. It may also be noted that the British Pharmacopœia expressly sanctions the substitution of arachis oil or sesame oil, *but no other oil or fat,* for olive oil, in India and in the eastern, African, and Australasian divisons of the Empire in making such preparations as camphorated oil, lead plaster, resin ointment, and other liniments, plasters, ointments, and soaps, in which the use of olive oil is directed.

*Apricot Kernel Oil.*—It is possible that, if the price allowed, apricot kernel oil would be preferred to pea-nut oil where the character of the oil employed is not subject to restrictions. The price of apricot kernel oil, however, is 3s. 9d. per lb., while pea-nut oil is obtainable at 1s. 7d. per lb., so that, for the present, this substitution is out of the question.

The oil may be obtained by crushing and grinding the entire seeds of the apricot—kernel and shell together—and then pressing for extraction of the oil. This extraction may be aided by the application of heat or the addition of water, or both.

About fifteen years ago, Messrs. Stafford Allen & Sons, of Finsbury, London, who claimed to have been the first to introduce British-pressed oil of peach or apricot kernels, stated that the apricot (*Prunus armeniaca*) rather than the peach (*Amygdalus persica*) had become the chief source of the oil, and they, thereforre, suggested that the confusion referred to at the commencement of the present article would be lessened by altering the name of peach (or apricot) kernel oil from *Oleum amygdalae persicae* to *Oleum pruni armeniacae.* Apricot kernels contain from 40 to 45 per cent of this fixed oil, which is used as an edible oil, in addition to replacing almond oil.

Some nine months ago it was observed that the Wellington Preserving Co. was advertising for sale large quantities of apricot stones. In order to ascertain the proportion of oil likely to be yielded by these stones and also the physical contents of such oil, and to compare these with recorded analyses of apricot kernel oil from elsewhere, a bag of these stones was very kindly supplied by the company at my request. The kernels were shelled and the oil, obtained both by cold expression at a pressure of two tons per square inch, and by ether extraction, was duly examined in this laboratory by Mr. W. J. Copenhagen.

*Laboratory Test of Apricot Kernels.*—The following tables show the results arrived at :—

| | Grms. |
|---|---|
| Average weight of apricot stone .. .. ... | 2·22 |
| Average weight of kernel ... .. ... ... | 0·47 |
| Percentage of kernel in stone ... .. ... | 21·35 |

The kernels, freed from shell, were analysed, with the following percentage results :—

| | In Fresh Kernels. | In Dried Kernels. |
|---|---|---|
| Moisture ... ... ... ... ... ... | 7·08 | — |
| Ash ... ... ... ... ... ... ... | 3·10 | 3·34 |
| Proteins (N×6·25) ... ... ... | 24·39 | 26·25 |
| Oil ... ... ... ... ... ... ... | 35·28 | 37·07 |

The following constants were obtained on examination of the oil :—

| | |
|---|---|
| Specific gravity at $\frac{15.5^\circ C}{15.5^\circ C}$ ... ... ... | 0·9211 |
| Saponification value .. ... ... ... .. ... | 179·0 |
| Acid value ... ... ... ... .. ... . | 1·83 |
| Refractive index at 40° C. (Z.B.R. 58·0) | 1·4646 |
| Iodine value ... ... .. ... .. .. | 112·0 |

The percentages of oil above recorded were obtained by ether extraction, but it is evident that cold expression would be a more suitable process, although yielding less oil. Apricot kernel oil, after having been pressed out and allowed to clarify by settling, is almost colourless, but gradually acquires a yellow colour. Its flavour is mild and pleasant. Messrs. Stafford Allen & Sons stated that peach kernel oil was originally imported into Britain from the Continent, and competed in price with true almond oil until its real nature was discovered (*Chemist and Druggist,* Feb. 11, 1905, p. 257). They pointed out that while oil of peach or apricot kernels is a genuine article of its kind, and may be legitimately employed, its surreptitious substitution for almond oil should be discountenanced.

*Constants of the Fixed Oils.*—It may be well, before passing over from the consideration of the fixed to the volatile oils, to quote some comparative figures arrived at on examination of the fixed oils of the almond, peach, and apricot.

The 1914 British Pharmacopœia lays down the following limits for almond oil :—

| | |
|---|---|
| Specific gravity ... ... ... | 0·915 to 0·920 |
| Saponification value ... ... | 188·0 to 196·0 |
| Acid value ... ... ... ... | under 6·0 |
| Refractive index (40° C.) ... | 1·4624 to 1·4640 |
| Iodine value ... ... ... ... | 93·0 to 100·0 |

Andes ("Vegetable Fats and Oils," p. 139) quotes the following constants :—

| | Almond Oil. | Apricot Oil |
|---|---|---|
| Specific gravity (15° C.) | 0·917- 0·920 | 0·915 |
| Saponification value | 187·9 -195·4 | 192·9 |
| Iodine value ... ... | 90·4 | 100·0 |

Apricot kernel oil, according to Andes, sets at −14° C., while almond oil sets only at −25° C. (−20° C. according to the United States Dispensatory).

Comparing the fixed oil of almonds with that of pea-nuts, Fryer and Weston ("Oils, Fats, and Waxes") give the following averages :—

| | Almond Oil | Arachis Oil. |
|---|---|---|
| Specific gravity (15·5° C.) ... | 0·918 | 0·9175 |
| Acid value ... .. ... ... | — | 10·0 |
| Saponification value ... ... | 192·0 | 193·0 |
| Iodine value ... ... ... ... | 99·0 | 90·0 |
| Refractive index (40° C., Z.B.R.) | 57·0 | 55·5 |
| Solidifying point of fatty acids | 10·5 | 28·5 |

The maxima and minima iodine values, according to the same authors, are as follows :—

| | |
|---|---|
| Almond oil ... ... ... ... ... ... ... | 98—100 |
| Peach oil .. ... ... ... ... ... ... | 92—109 |
| Apricot oil ... ... ... ... ... ... ... | 101—108 |

Rogers ("Elements of Industrial Chemistry")

gives the following comparative table :—

| | Almond | Peach Kernel. |
|---|---|---|
| Oil content of seed | 45-55 p. cent | 32-35 p. cent |
| Specific gravity of oil | 0·9175-0·9195 | 0·9180-0·9215 |
| Refractive index ... | 1·4731- (15·5° C.) | 1·4713 (15° C.) |
| Iodine value . . . | 100·7 | 92·3-100·3 |

Lewkowitsch gives the following constants of apricot kernel oil. No. 2 being from Mogador, and No. 3 from Californian kernels :—

| | 1. | 2. | 3. |
|---|---|---|---|
| Specific gravity ... | 0·9200 | 0·9172 | 0·9203 |
| Saponification value | 192·4 | 198·2 | 190·3 |
| Acid value . . . . | 2·3 | 2·8 | 1·2 |
| Refractive index (40° C., Z.B.R.) | 58·0 | 57 0 | 58·0 |
| Iodine value . . . . | 107·4 | 107·9 | 108·7 |

The following comparative table is compiled from Allen's "Commercial Organic Analysis" :—

| | Almond Oil. | Peach Oil. | Apricot Oil. |
|---|---|---|---|
| Specific gravity 15° to 15·5° C. | 0·914-0·920 | 0·918-0·920 | 0·918-0·920 |
| Saponification value ... | 287-294 | 293-297 | 291 |
| Iodine value | 93-101·9 | 92·5-99·7 | 100-108 |

*The Essential Oils.*—The volatile or essential oils, both of the bitter almond as well as of the peach or apricot (sweet almonds, it will be borne in mind, do not yield an essential oil), are derived from their respective sources by processes wholly different from, and subsequent to, those by which the fixed oils are obtained. It is only on treating with water the cake or marc remaining after expressing the fixed oil, leaving it to macerate for 24 hours or more, and then subjecting the mash to distillation, that the volatile oils are obtained. This process, as indicated above, can be applied to either almonds, peach, or apricot kernels, for in all three cases the glucoside amygdalin and the ferment emulsin are present, and so benzaldehyde and hydrocyanic acid are formed and distil over when heat is applied. Bitter almonds yield from 1 to 3 per cent of this essential oil. The South African apricot kernels yielded 0·5 per cent.

In the case of apricots the residual cake has been used for feeding poultry and in the manufacture of liqueur.

The following are the characteristic constants of bitter (*i.e.,* essential) almond oil, with and without hydrocyanic acid, according to Parry ("Chemistry of Essential Oils") :—

| | Containing Acid. | Freed from Acid. |
|---|---|---|
| Specific gravity ... ... | 1·045-1·070 | 1·049-1·055 |
| Refractive index ... | 1·532-1·545 | 1·542-1·546 |

High specific gravity usually indicates the presence of a large amount of hydrocyanic acid, and hence a particularly poisonous oil. These essential oils are much used for flavouring purposes in cookery, and in order to enable them to be so used with safety, they are freed from the extremely poisonous hydrocyanic acid (or prussic acid, as it used to be called), which is present in the distilled essential oil to the extent of about 5 or 6 per cent, or 13 per cent according to the U.S. National Dispensatory. The purification of the essential oil is effected by redistilling it over ferrous hydroxide, that is to say, a mixture of lime and ferrous sulphate. So it comes about that two varieties of the essential oils are on the market, one variety containing, and the other freed, from hydrocyanic acid. These two varieties must be most carefully distinguished from each other on account of the very poisonous character of the one. The bitter almond oil freed from hydrocyanic acid is known in the drug trade as "Essential Oil of Almonds, S.A.P." (*i.e., sine acido prussico*). That containing the hydrocyanic acid is, on account of its fairly stable composition, regarded as one of the best forms in which that powerful drug can be administered.

The benzaldehyde, which is the main constituent of the essential oil, gradually absorbs oxygen from the air and changes into benzoic acid, which in course of time appears as a crystalline deposit in the oil, and may accumulate to such an extent as to impart to the oil a semi-solid character.

Artificial oil of bitter almonds is simply benzaldehyde prepared synthetically from the hydrocarbon toluene, one of the products of the destructive distillation of coal, hydrocyanic acid being frequently added to bring it within pharmacopœa requirements.

Essential oil of bitter almonds has been frequently adulterated with or even wholly replaced by synthetic benzaldehyde prepared from toluene. For this purpose toluene is oxidised, according to a German patent which has been successfully worked, by means of nickel or cobalt oxide. This synthetic oil is practically as good a flavouring as the genuine essential oil, but it oxidises more rapidly.

In concluson, it will be of interest to record that towards the close of last year a Rotterdam firm made inquiries in Souh Africa for apricot kernels, which they were prepared to purchase at £70 per ton.—*The South African Journal of Industries.*

## CHEMICAL RESEARCH FOR THE DEVELOPMENT OF INDUSTRIES IN INDIA.*

By E. R. WATSON, M.A., D.Sc,
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Having recently been entrusted with the task of starting a research institute for the Government of the United Provinces, I have naturally been giving considerable attention to the question as to what chemical researches are likely to be most useful for the development of industries in that Province. And as I have been prevented by the circumstances of the case from doing much experimental work, I thought I could not do better, when I was asked to open a discussion at the Indian Science Congress on a chemical subject, than invite discussion on the same subject, widening the field to the whole of India. At any rate, I feel sure that I am opening a discussion on a subject or group of subjects which is of great interest to many members, and I hope that I shall

*An Address read at the Calcutta Meeting of the Indian Science Congress, on February 1, 1921.

learn a great deal from the discussion which will follow.

On attempting to answer the question I have proposed, viz., what chemical researches are most urgently required and most likely to lead to important industrial developments in India, one feels that a somewhat wider question must first be tackled; namely, what industries involving chemistry are most capable of development or likely to develop in India. The two problems are not synonymous, as there may be industries involving chemistry which are capable of large and successful development in this country without the assistance of chemical research or with very little assistance. Again, this second question, as to what industries involving chemistry are capable of development, is evidently part of a still wider question, viz., that of the industrial development of India as a whole. I do not intend rigidly to separate these different questions. My object is to promote useful discussion.

I should like first to mention the chief contributions which have already been made to this subject. The United Provinces Government was early in the field, as in 1907 it considered the establishment of a technological institute at Cawnpore, of which one of the main functions was to be chemical research for the promotion of industries: and in several official communications it gave its views as to what chemical researches were most urgently required and most likely to be useful.

The Industrial Commission's report (1918) has a chapter on the deficiencies in Indian industries. It points out the order in which industries have developed in other countries, viz., iron and steel manufacture first, then the production of textiles and similar goods by machinery, then the manufacture of chemicals required in these large-scale industries. It points out India's deficiency in iron and steel production which has retarded the proper development of many industries dependent on machinery. It says, "the incompleteness of our existing system of industries has been brought into prominent notice by the interference with industrial supplies from overseas due to the war. This constitutes a serious natural danger, the extent and gravity of which will be more clearly realised if we refer in detail to some of the more important manufactured materials or articles which are not at present made in India, although the basis for their production exists in the form of raw materials." The following materials and articles are then mentioned: zinc, copper, tungsten, and other ingredients of high-speed steels, chromium, graphite, thorium salts for incandescent mantles, caustic soda, benzol and related products, rubber goods, tin plate, paper, drugs, dyes, essential oils. It is remarked that "in the absence of any means for producing from purely Indian sources, sulphuric, nitric, and hydrochloric acids and alkalis, our manufactures, actual or prospective, of paper, drugs, matches, oils, explosives, disinfectants, dyes, and textiles are dependent upon imports which under war conditions might be cut off." Yet "sources of raw materials for heavy chemicals are not deficient."

Drs Sudborough and Simonsen have discussed chemical industries in the late Indian Munitions Board's Industrial Handbook (1919). They there laid down the general principle that in any attempts to foster the development of chemical industries in India, attention should be directed, in the first instance, to industries which make use of the Indian-grown raw materials now exported to other countries. Included in these exports are (1) the raw materials from which important fixed oils and feeding cakes are manufactured; (2) the raw materials from which valuable essential oils and medicinal drugs are prepared; and (3) various mineral products, such as chrome, manganese, and zinc ores, wolfram, and monazite sands. It is, however, admitted that the proposition of making India an oil and oil-products exporting, rather than an oil-seeds exporting, country is not a simple one. In addition to such industries, it is recognised that the manufacture of heavy chemicals is a key industry or group of key industries; and, as to their prospects, it is considered, firstly, that the manufacture of sulphuric acid from zinc concentrates is promising; secondly that sufficient nitric acid for some time to come can suitably be obtained from Indian nitre (the utilisation of atmospheric nitrogen is considered to be a proposition requiring careful consideration), and, thirdly, that it is doubtful whether sufficient soda to meet all Indian requirements can be obtained by the extraction of alkaline soils. The cost of the ammonia soda process would probably be too heavy to permit of soda manufactured by this process competing with imported carbonate in normal times. The electrolytic production of caustic soda and soda ash could only be made a success by utilising the bye-products, and Magadi soda is likely to be a dangerous competitor with the Indian manufactured article; but, nevertheless, alkalis are so important that it may be necessary to protect their manufacture. It is considered essential to manufacture chlorine and bleaching powder in India.

As to the manufacture of explosives, synthetic dyes, drugs, &c., from coal-tar, it is considered that the amounts of tar available in India at present are quite insufficient to start a large coal-tar industry, and that the only way to start such an industry would be to coke all suitable coal at the pithead.

The manufacture of permanganates, chromates, and lead products, such as litharge, red lead, and white lead, are all considered to be eminently practical propositions.

Wood distillation is regarded as rather a doubtful proposition, owing to the existence of large supplies of its products and the low prices likely to prevail for some time after the war.

The Indian Munitions Board held a conference of chemists in 1918 and organised as far as possible chemical research work on industrial problems. Their list of chemical researches which have been taken up includes very little under the head of heavy chemicals; it includes a good many researches on Indian oils, such as *neem*, *mahva*, *til*, fish oils, the hardening of oils, the manufacture of glycerin and varnishes, the utilisation of new Indian tanning materials and preparation of tanning extracts; the preparation and refining of essential oils, such as rose, patchouli, retivert, lemon-grass, clove, cardamom; the manufacture of strychnine, atropine, and caffeine, the manufacture of chromates, wood-distillation, and various problems which are not touched on in the Handbook, such as

the manufacture of starch, alcohol, and glue.

The Chemical Services Committee (1919-20) have expressed the opinion that India is deficient at present in raw materials for the production of organic chemicals from coal, but consider that there is an enormous field for the production of carbon compounds from vegetable products. They explain that they do not only refer to such products as oils from oil-seeds, indigenous dyes, drugs, and essential oils, but consider that there is a great field for the production of new products of greater economic value by the conversion of organic compounds present in Indian plants.

From these references to what has already been said on the subject it is obvious that the subject can be looked at from several points of view. In the first place, it may be argued that, as India is essentially an agricultural country, exporting large quantites of agricultural products, the most obvious industrial development is to carry out in this country the processes to which those products are at present submitted on arrival at their destination. This argument recommends the pressing of oil seeds, the manufacture of soap, glycerin, and varnishes, the tanning of hides and skins, the extraction of alkaloids and so on. In the second place, it may be argued that industries are bound to develop in all countries according to a definite sequence; iron and steel first, then machinery, then the textile and similar industries, and then the chemical industries to meet the requirements of these. In the third place, the great war has brought into prominence the disadvantage at which a country may be placed unless it is self-supporting as regards essentials, such as food and clothing and munitions of war. From this point of view it may be necessary for the State to protect and foster certain key industries.

At first sight it appears as though these different arguments might lead to different recommendations as to the chemical industries which should first be developed in India. If this is the case, it is obvious that there is something wrong with one or other of these general principles. But I think I shall be able to show that when carried to a conclusion all the arguments lead to the same recommendations. My own employment during the war, when I had the pleasure of helping in the British manufacture of synthetic dyes, naturally makes me inclined to look on the problem of Indian industrial development from the last point of view, viz., to see that key industries are placed on a satisfactory footing. Fortunately, India is essentially self-contained as regards foodstuffs and textile fibres; but she is by no means self-contained as regards military requirements, such as explosives and synthetic dyes. This points to the desirability of establishing the coal-tar industry in this country; for it is from coal-tar that all countries obtain high explosives, their synthetic drugs and their synthetic dyes. The war has taught us how intimately inter-connected are the manufacture of these three groups of chemical products. I find, however, that most chemists who have given their attention to the development of Indian industries discourage the idea of attempting the manufacture of explosives, drugs, and dyes from coal-tar. They say India does not produce sufficient tar; the tar is deficient in the most valuable ingredients; it is doubtful whether England will succeed in manufacturing these products in the face of German competition, and so it would obviously be absurd for India to try.

Let us take first the most obvious military necessity, viz., explosives. What quantity of explosives does India consume? What quantity is she likely to require in the event of war? How much does she manufacture at present and how much does she import? I have not got any official returns as to production and consumption, but I calculate that India is producing less (probably far less) than 4000 tons of explosives annually, and importing less (probably far less) than 5000 tons. I have arrived at the figure for India's production of explosives from the total consumption of nitrates and nitric acid in the country. The majority of the nitrates are no doubt used as manures, so that my figure is the maximum possible, which is probably many times greater than the actual. And for India's imports of explosives I have had to go by the figures for imports of explosives as private merchandise *plus* total Government import of arms, ammunition, and military stores, excluding firearms. Here, again, my figure is the outside limit which is probably far greater than the actual figure. But these figures are no higher than the most moderate estimate of India's probable requirements in the case of war. Before the war England produced 18,000 tons of explosives annually. By 1916 the amount had risen to 200,000 tons, and by the end of the war to about 350,000 tons. As we are on the subject of coal-tar, let us consider first those explosives which are manufactured from coal-tar, *i.e.*, high explosives, such as picric acid and T.N.T. Ammonium nitrate is also very important and can also be manufactured in connection with the coal-distillation industry. During the war England produced about 1,500 tons of picric acid and T.N.T. a week, as compared with 2500 tons of propellants, such as cordite, and 3000 tons of ammonium nitrate. As a most modest estimate, we may assume that India should be able to produce 4000 tons of picric acid and T.N.T. per annum, and might require many times that amount.

At present India makes about 500,000 tons of coke and 8000 tons of tar per annum. It is estimated that, if all the coke were manufactured in bye-product recovering plants, about 16,000 tons of tar would become available. This is a low figure, based on a note prepared by Mr. W. J. Alcock for the Indian Munitions Board. I think it is probably based on practice in the Bengal Iron and Steel Company's coking plant. It is well-known that the yield of tar depends very much on conditions of coking, so that too much importance should not be attached to the low yield. But as the benzene and toluene content of tar is only about 1 per cent, we could not get more than 80 tons of benzene and toluene a year if all the tar at present produced were distilled for this purpose. The amounts of tar available in India under present conditions are obviously quite insufficient to produce all the explosives required. But Drs. Sudborough and Simonsen estimate that, if scrubbing plant for recovering benzene and toluene from the coke-oven gases were introduced, an additional 2,000,000 gallons, or about 10,000 tons, of crude benzol could be obtained. With this quantity of crude benzol available, the manufacture of high explosives be-

comes a practical proposition. Drs. Sudborough and Simonsen's estimate of 10,000 tons of crude benzol from plant producing 500,000 tons of coke is high, but, even during the war, the yield of crude benzol has been much increased by improved washing. According to the *Proceedings of the Institute of Civil Engineers* for March, 1918, 13·5lb. of benzene and toluene can be obtained from one ton of coal. Calculating from this figure, plant producing 500,000 tons of coke could yield nine million pounds, or about one million gallons, of benzene and toluene. This quantity of benzene and toluene would suffice to produce the quantity of explosive which we calculated as India's minimum safe production. In peace these hydrocarbons could be utilised largely for the production of dyestuffs. The Germans showed during the war the close connection between the manufacture of explosives and synthetic dyes and drugs. Plant used in peace time for manufacturing dyes can readily be turned in war time to the production of explosives. Germany's large dye manufacturing concerns were so employed during the war. India's maximum annual importation of dyestuffs was 8000 tons. This is a figure of about the same order as her requirements in the way of explosives and her present productive capacity in the way of benzene and toluene from her coking operations. Her production of iron and steel is bound to increase. Her coal resources have not yet been fully exploited and she already produces 20 million tons per annum. The amount of iron ore and other requisites for iron and steel manufacture are unlimited. India produces at present about 250,000 tons of iron and steel and imports 1¼ million tons annually. If she produced only as much as she now requires the blast furnaces would consume at least 1¼ million tons of coke, and this would at once triple the possible production of benzene and toluene.

My calculations may be wrong, but so far as benzene and toluene are concerned, I think India is in a sound position to undertake the manufacture of explosives, synthetic dyes, and drugs.

Nor is India by any means dependent on her coking ovens for a sufficient supply of aromatic hydrocarbons to manufacture all the explosives and synthetic dyes she may need. During the war a good deal of attention was given to the production of these hydrocarbons from petroleum, and it is now recognised that this is a practical proposition. Ordinary scientific literature contains very little information on the subject. But in 1907 Jones and Wootton pointed out in the *Transactions of the Chemical Society* that Borneo petroleum contains a considerable quantity of aromatic hydrocarbons, and we learn from a paper in the *Journal of the Society of Chemical Industry*, 1919, that a source of supply of toluene for British explosives was developed during the war by the Asiatic Petroleum Co. from Borneo spirit. The third volume of the Society of Chemical Industries' Annual Reports informs us that in Russia aromatic hydrocarbons for dyes and explosives have long been obtained by cracking petroleum oils. Nikiforoff took out patents on this subject in 1886, 1887, 1901, and 1902. In the United States of America, also, a great deal of attention was paid during the war to the production of aromatic hydrocarbons by cracking petroleum.

Mention has already been made of the Chemical Services Committee's suggestion that some of the numerous organic compounds produced so freely in the vegetable world in India could be subjected to a variety of chemical processes to yield a range of chemical products. Explosives and dyes might be produced in this way, *e.g.*, tannins are produced in India in enormous quantities in barks, fruits, &c. Ordinary tannin or tannic acid is converted quantitatively into gallic acid on hydrolysis. Gallic acid is said to be converted quantitatively into salicylic acid or benzoic acid by reduction with zinc dust and ammonia (Guignet, *Bulletin de la Société Chimique*, (3), 7,153). These substances might serve as starting-out materials for the preparation of explosives, dyes, &c. I do not wish to be more explicit at present, but I may say that experiments I have in hand have already shown that aromatic hydrocarbons, ample for India's requirements in the way of explosives, dyes, and drugs, can be obtained conveniently and cheaply from indigenous materials other than coal distillation bye-products. I hope shortly to patent these methods of production and get them taken up on a large scale. Private firms of explosive manufacturers have already been considering the manufacture of high explosives in India.

It may, however, be argued that the successful manufacture of explosives, synthetic dyes, and drugs, requires not only a sufficient supply of cheap aromatic hydrocarbons but many other chemicals in considerable quantity, such as sulphuric acid, nitric acid, caustic soda, alcohol, wood spirit, formaldehyde, chlorine, nitrite, zinc, ammonia, &c., and that the want of these renders impracticable any proposition for manufacturing dyes and explosives in India. Let us consider these chemicals in detail.

*Sulphuric Acid.*—The manufacture of this acid has up to the present been seriously handicapped by the absence of suitable sulphides for roasting, and imported sulphuric has been used. India's present consumption of sulphuric acid is somewhere between 10 and 40 thousand tons per annum.

Owing to the importance both of sulphuric acid and zinc "the Government of India is interesting itself in the proposal to erect zinc-smelting works at Jamshedpur, where the zinc concentrates from Bawdwin in Burma will be dealt with and the spelter and sulphuric acid yielded made available to the Tata Iron and Steel Co. for their own purposes and for subsidiary companies. The plant, which it is proposed to erect with a loan from Government, will be capable of dealing with 25,000 tons of zinc concentrates, and the estimated output is 10,000 tons of spelter per annum" (Cotton, "Handbook of Commercial Information for India," p. 234) and 32,000 tons of sulphuric acid. The iron and steel industry requires large quantities of sulphuric acid for recovering ammonia from the coking plant and for pickling iron plate for galvanising and tinning. Most countries consume very large quantities in the manufacture of superphosphates. There is no reason to fear that the production of sulphuric acid will exceed the demand, but it should meet all requirements for some time, including requirements for the manufacture of explosives and

dyes. I have no information as to the amount of zinc concentrate which may eventually become available. At present this scheme has a serious defect from the military point of view, as a blockade of the Bay of Bengal would cut off the supplies of zinc concentrates. A railway from Burma to India is in contemplation, but I do not know whether it is likely to be built immediately. It seems remarkable that it should be necessary to go over-seas, even as far as Burma, for sufficient suitable sulphur compounds for the manufacture of sulphuric acid. During the war the German Government is said to have subsidised heavily an enterprise for the manufacture of sulphuric acid from gypsum (*Journal Soc. Chem. Indus.*, 1916, 1058; U.S. Pat. 1197331, Sept. 5, 1916), and it is stated that sulphuric acid can be manufactured in any quantity by this process at the same cost as from imported pyrites. On consideration, it seems almost certain that in any country the bulk of the element sulphur will be in the form of sulphates. Sulphides are essentially unstable compounds, and on weathering are converted with sulphates. It is certain that there are sufficient natural sulphates in India to supply all the sulphuric acid likely to be required either now or in the future. I hope shortly to take out patents for the manufacture of sulphuric acid from readily available natural sulphates.

*Nitric Acid.*—At present India exports about 26,000 tons of nitre, consumes about 4000 tons, and imports about 1700 tons of Chili saltpetre. Her imports of nitric acid are negligible. With a sufficient supply of sulphuric acid there will be no difficulty about producing the nitric acid required for explosives and dyes.

*Caustic Soda.*—The quantity of alkalis required for the manufacture of dyes and explosives is comparatively small, and India's requirements in this respect could easily be met from the salts contained in alkaline soils. Drs. Sudborough and Simonsen's remarks on the question of alkali manufacture have already been quoted at some length. That it is a key industry there can be no question. The present consumption of alkalis is comparatively small (35,000 tons of soda imported in 1917-18) but increased production of cotton goods and soap is bound to multiply many times the present demand for alkalis. An increased demand for cotton goods is one of the most certain results of India's development, and, with an increase in the production of iron and steel and machinery, there is no doubt that increasing quantities of cotton goods will be manufactured in this country. The present value of cotton goods consumed per head of the population is Rs.2-12 per annum. There can be no doubt that this will be multiplied several times in the near future, and that the bulk of the goods will be manufactured in this country. This will increase proportionately the demand for alkalis, which are used for scouring cotton goods.

It is doubful whether it will be feasible to get all the alkalis required from alkaline soils. Mr. Srivastava, Industrial Chemist to the United Provinces Government, estimated that 5000 tons of soda ash per annum could easily be obtained from *reh* soils near Cawnpore. There are large tracts of such soils in the United Provinces and the Punjab, and there would be no difficulty in manufacturing all India's alkali requirements from these soils if Mr. Srivastava's estimate is correct. On the other hand, I hear that a recent survey by the Geological Department of the alkaline earths of Rajputana gave disappointing results, although these soils have generally been considered a more suitable source of soda than the soils of the United Provinces and the Punjab. Some more quantitative information about the alkaline soils of the United Provices and the Punjab is urgently required to decide the lines on which this key industry must develop.

*Alcohol.*—As India is essentially an agricultural country and exports large quantities of material, such as grain, which are used in the country of destination for the production of alcohol, there seems no reason to doubt that industrial alcohol could be successfully produced in India. Dr. Fowler's selection of *mahua* flowers as the most suitable starting-out material has been criticised, but I have not time at present to discuss his point.

*Wood Spirit, Formaldehyde, and Acetic Acid.*—I have already mentioned that the writers of the article on chemical industries in the late Indian Munitions Board's Handbook look on wood-distillation in India as a somewhat doubtful proposition, on the ground that very large plants for wood-distillation were set up for war purposes and will flood the post-war market with wood spirit and acetic acid at low prices. But these products are all dangerous chemicals, and shipping freights on them are very high, so that a comparatively small plant meeting India's requirements would possibly be a sound proposition, although manufacture on a large scale for export might not be feasible.

I hope I have said enough to show that we do not really arrive at different conclusions by approaching from different points of view the problem of the development of India's chemical industries. If we start with the idea that the first and most obvious thing to do is to work up our vegetable products to a certain extent before export, we find that to do this we want cheap acid, alkalis, spirit, &c. If we start with the idea that there is only one possible sequence of development of industries which has been followed in all countries which have developed, and must be followed in all countries which are developing, viz., iron and steel manufacture first, then machinery, then textiles, &c., with chemical industries as hand-maidens called in as required, we find again that cheap acids and alkalis are the first chemical requirements, and the manufacture of explosives, dyes, and drugs, necessarily follows for the utilization of by-products and to meet the requirements of the textile industry. If we start with the idea that first and foremost we must see that India's military requirements are met so that she could withstand a blockade, then we decide that explosives must be manufactured in the country from materials all available in the country. This leads again to the necessity for developing the iron and steel industry, for the manufacture of acids and alkalis, the utilisation of coking bye-products and the manufacture of dyes and drugs along with the explosives.

I find that I have spoken chiefly about the development of chemical industries in India and

very little about chemical research for the development of industries. But that seems to me the proper way of looking at the subject. First let us decide what has to be done, and then let us see how chemical research may assist. At first it may seem that there is not much need for research to instal in India such well-known industries as the manufacture of iron and steel, sulphuric acid, alkalis, coking bye-products, &c. But my discussion of these problems has already suggested several researches, *e.g.*, the question of the utilisation of sulphates for the manufacture of sulphuric acid, a survey of India's alkaline soils, and the possibility of finding other sources than coal-tar and coke-oven bye-products for the manufacture of aromatic compounds, such as explosives, dyes, and drugs. These are researches for the decision of most important and fundamental questions. The establishment of any manufacture involving chemical reactions on a large scale is much assisted by chemical research.

Problems are certain to arise from the fact that the materials available, or climatic conditions, or other factors, are different from those in the countries already carrying on these manufactures These are platitudes which the British find it hard to recognise, but which are, nevertheless, recognised to a greater extent than before the war. So far I have spoken of research in connection with the fundamental industries. For others which are not, perhaps, of such vital importance, there are any number of chemical problems appealing, perhaps, more strongly to the chemist, whose interests are primarily scientific, *e.g.*, lac-dye is thrown away at the present time. Apparently the fastness to alkalies of its dyeings is not quite good enough to meet modern requirements, but it is an anthraquinone derivative, and so belongs to the same family as our most valuable mordant and vat dyes. Comparatively simple chemical treatment might convert it into a valuable dye. In Indian turpentine we have a cheap source of pinene in any quantity. The chemical relationship between the different members of the terpene group is very close, and it seems quite feasible to convert pinene into the unsaturated-open chain compounds which are the chief constituents of essential oils and perfumes. Amongst the vegetable products of India the organic chemist can find any number of problems of interest, and very likely of profit.—*Journal of Indian Industries and Labour*

## NEW BRITISH CHEMICAL STANDARDS
(ANALYTICALLY STANDARDISED SAMPLES).

ANOTHER new plain carbon steel is now ready for issue, viz., "R," which fills the vacancy in the series for a carbon standard between "I" (carbon 0·521 per cent) and 'SI" (carbon 0·921 per cent). It is also intended to serve as a high manganese standard and a sulphur standard in high carbon steel. The analyses have been undertaken as usual by a number of experienced chemists representing the following interests: British Government Dept.; U.S. Bureau of Standards; Referee Analysts, independent; Railway Analysts, representing users issuing specifications; Works Analysts, representing makers and users.

The standard figures are as follows:—

*Carbon Steel "R."*

| | |
|---|---|
| Carbon (combustion) ... ... .. | 0·786 |
| Carbon (colorimetric) ... .. ... | 0·790 |
| Silicon ... ... ... ... .. ... | 0·22* |
| Sulphur, total by oxidation .. | 0·053 |
| Sulphur, evolved as sulphide .. | 0·050 |
| Phosphorus ... ... ... . . ... | 0·058* |
| Manganese .. ... ... ... ... | 0·914 |
| Arsenic ... ... ... ... ... ... | 0·03* |
| Copper ... ... ... ... ... ... | 0·02* |
| Ni, Cr, W, Mo ... | None detected by qualitative tests. |

* Approximate.

The standards may be obtained in 500, 100, or 50 grm. bottles, either direct from Organising Headquarters, 3, Wilson Street, Middlesbrough; or through any of the leading laboratory furnishers at a price just sufficient to cover the cost. A certificate giving the names of the analysts cooperating, the types of methods used, and a detailed list of the results will be supplied with each bottle.

## NOTICES OF BOOKS.

*Technical Methods of Analysis.* Edited by ROGER CASTLE GRIFFIN. First Edition. Pp. xv.+ 666. London: McGraw-Hill Book Co. Inc. Price 33s.

This book contains a comprehensive selection of practical methods of analysis which have, with a few exceptions, been tested and adopted in the laboratories of Arthur D. Little, Inc., one of the best-known firms of consulting chemists in the United States.

Some of the methods described are original, but most of them are already well-known, many of these, however, have been more or less modified in the light of experience gained through many years of practice. After dealing with the methods of preparation and the strengths of reagents, volumetric solutions and indicators, there follow chapters on the analysis of inorganic and organic materials of a general nature. These are followed by chapters each dealing with a special class of materials such as metals, fuels, paints, oils, wood and paper, textiles, and foodstuffs.

Miscellaneous analyses include such materials as case-hardening compounds, metal polishes, and road-making materials.

Analyses of drugs, alkaloids, minerals, &c., which are generally dealt with by specialists in these particular branches of chemistry are not included in the book, which is intended for those engaged more in the general run of work in a commercial laboratory.

The methods are described in a direct and practical manner, no attempt having been made to prove their accuracy by means of experimental data nor to explain the theory of the procedure.

The book is completed by a series of analytical tables newly calculated from the 1920 International Atomic Weights, and a good bibliography of books and pamphlets which has been found to be of great value in the laboratory.

*Fundamental Principles of Organic Chemistry.* By CHARLES MOUREU, Member of the Institute and of the Academy of Medicine, Professor at the College de France. Authorised translation from the Sixth French Edition by WALTER T. K. BRAUNHOLTZ, B.A., A.I.C. With an introduction by Sir WILLIAM J. POPE, K.B.E., F.R.S. London: G. Bell & Sons, Sons, Ltd. Price 12s. 6d. net.

In the introduction by Sir William Pope, it is stated that the student who desires an intelligent acquainance with Organic Chemistry must be so steeped in the various modes of presentation of the subject, guiding principles become an instinct with him, and that bias toward the adoption of any specific classificatory system disappears. For this reason the translation of the work of Prof. Moureu, who is one of the foremost of French organic chemists, will be welcomed by English students.

The work of the author has been fully appreciated in France, having run into six editions within a very short time. The translator draws attention to the fact hat he has very closely followed he sixth edition, except in the mater of nomenclature, substituting the English system for that of the Geneva Congress, which is largely used in the original. The author's method of teaching and his individuality is by no means lost in the translation.

In spite of the magnitude of the subject, the work is encompassed in less than 400 pages, and is well printed by William Clowes & Co.

## CORRESPONDENCE.

### THE BATTLE OF JUTLAND FILM.

*To the Editor of the Chemical News.*

SIR,—A number of cinema proprietors, who are about to show above picture, are desirous of engaging the services of Jutland survivors who are willing to speak to the film when it is being exhibited. As proprietors of the picture in question, we are prepared to make a register of all such men, if they will be good enough to send us their names and addresses as well as their rank and the name of their ship. We will put them in touch, in each case, with the nearest cinemas showing the picture.

As this is the only means we have of reaching the survivors of the Battle, we shall esteem it a great favour if you would be so good as to grant us the courtesy of your columns.—I am, &c.,

H. ROWSON,
Managing Director, Ideal Films, Ltd.

## NOTES.

FARADAY SOCIETY.—A General Discussion on "Catalysis with special reference to Newer Theories of Chemical Action" will be held under the auspices of the Faraday Society, on Wednesday, September 28, at the Institution of Electrical Engineers, Victoria Embankment, W.C.2. The Discussion will be divided into two parts: Part I. beginning at 4.30 p.m., will deal with the "Radiation Theory of Chemical Action," and it will be opened by Prof. J. Perrin, of Paris. The second portion of the Discusson will concern itself with "Heterogeneous Reactions," and it will be opened by Prof. Irving Langmuir, Chief Research Chemist to the General Electric Company, U.S.A. It is expected that Prof. Arrhenius and Prof. Victor Henri will also be present, and among others who will contribute to the Discussion are Prof. E. C. C. Baly, Prof. F. G. Donnan, Prof W. C. McC. Lewis, Prof. A. Lindemann, Prof. A. W. Porter, and Dr. E. K. Rideal. Fellows of the Chemical Society are invited to attend this meeting Others interested in the subject may obtain tickets of admission from the Secretary of the Faraday Society, 10, Essex Street, London, W.C.2.

NORTHAMPTON POLYTECHNIC INSTITUTE.—The new session in the evening courses and classes will start on September 26, and the day courses and classes a week later. The entrance examinations for the latter will be held on the 27th and 28th instants. Last session marked the resumption of full work in all departments of the Polytechnic on the conclusion of the war. The enrolments being more numerous, in all courses and classes than in any pre-war session, many applicants for evening work had to be placed on the waiting lists. It may now be taken that all the classes are in their full pre-war stride, only more so. Very substantial additions were made to the equipment during the last session, owing to a liberal grant of the London County Council. During the disturbance caused by the war, the equipment could not be kept up to its usual high and up-to-date standard, and although it cannot be said that in all directions the well-known character of the equipment has been resumed, a very good start has been made in supplying the deficiencies, both in the engineering departments proper, but more especially in the department of optical engineering, and applied optics. A further grant has been made by the London County Council, which will be expended during the current session in dealing with the most urgent needs.

X-RAYS IN INDUSTRY.—A correspondent of the *Manchester Guardian Commercial* in this week's issue refers to the use of X-rays in industry. He says the public know little of the manner in which Rontgen rays were made use of during the war in locating hidden defects in materials used for important purposes, such as the building of aeroplanes. At the moment industrial radiology is young, and care must be taken not to claim for it too much at such an early stage. Nevertheless, it has already shown that its possibilities outside the range of surgical applications are boundless, and for that reason the establishment of an Institute of Radiology in London is a project which deserves every possible support.

MR. S. HORWOOD TUCKER, M.Sc., has been appointed to the Lectureship in Organic Chemistry in the University of Glasgow.

SAFEGUARDING OF INDUSTRIES ACT.—In accordance with Section 7 of the Safeguarding of Industries Act, the President of the Board of Trade has appointed the following gentlemen to be members of the permanent panel from which Committees, consisting of five persons, will be selected from time to time to consider and report upon complaints referred to them by the Board under Part II. (Prevention of Dumping) of the Act: Sir W.

M. Acworth, J. Arthur Aiton, Esq., C.B.E., Sir William Ashley, Arthur Balfour, Esq., J.P., Sir George S. Barnes, K.C.B., K.C.S.I., Sir John N. Barran, Bt , J. T. Brownlie, Esq., Sir Cecil L. Budd, K.B.E., Sir James C. Calder, C.B.E , Dr. J. H. Clapham, O.B.E., T P. Cook, Esq., F. R. Davenport, Esq., A. K. Davies, Esq., F. P Dorizzi, Esq., Rayner Goddard, Esq., Sir E. C. K. Gonner, K.B.E., Sir George R. Lowndes, K.C.S.I., K.C., Prof D. H. Macgregor, Stanley Machin, Esq., J.P., G. A. Moore, Esq., J. W Murray, Esq., D.L., Sir Douglas Newton, K.B.E., Owen Parker, Esq., C.B.E , J.P., R. G. Perry, Esq., C.B.E., Arthur Pugh, Esq., Sir R. Henry Rew, K.C.B., C. A. Russell, Esq., K.C., Arthur Shaw, Esq., Sir Charles Stewart, K.B.E., Sir Edwin F. Stockton, J.P., H. L. Symonds, Esq., Gilbert C. Vyle, Esq., Sir Frank Warner, K.B.E.

PRICKLY-PEAR FRUIT.—The tuna, or prickly-pear fruit, is said to contain on an average about 10 per cent of sugar directly and completely fermentable into alcohol, and according to investigations carred on in the New Mexico College of Agriculture, a yield of 10 tons of fruit per acre was estimated, but the difficulty in the way of practical application was the lack of some economic method of collecting the fruit. Hand-picking is not considered sufficiently expeditious, and a machine for collecting large yields of fruit from small areas was looked upon as essential. The amount of sugar in the fruit may vary from 5 to 15 per cent, mainly in the form of reducing-sugar (dextrose). It has been found that fruit which contained 7 per cent of sugar in August (U.S.A.) increased its sugar-content within a month to 12 per cent. The theoretical yield of alcohol from 100 kilogrms. of dextrose is 51·1 kilogrms., corresponding to 64·4 litres, so that 10 tons of prickly-pear tunas, carrying 10 per cent of sugar, would yield 1022lb., or 128 gallons from one acre. Those who carried on the above investigation reckoned that the cost of producing alcohol from prickly-pear tunas would not exceed 7½d. per gallon in a distillery producing 500 gallons of 90 per cent alcohol per 24 hours. Estimating the cost of such a distillery at something over £3000, with a 10-years' life-period, its annual cost was put down as £625. A 60-day season would result in 30,000 gallons of 90 per cent alcohol, depreciation and interest being allowed for at 5d. per gallon of alcohol. For such a factory, assuming 100lb. of fruit to produce 5lb. of alcohol, 2100 tons of fruit would be needed during a two-months season, that is to say, the harvest of about 200 acres. From the above it would appear that between 140 and 150lb. of the tunas would yield 1 gallon of alcohol: at 1s. 8d. per gallon, 1 short ton of fruit would, therefore, be worth about 22s. for alcohol production. If 150lb. produce 1 gallon at the above price, about 8½d. would be available to pay for every 100lb. of fruit and for manufacturer's profits. If the fruit cost 7½d. per 100lb., the fermentation of 2100 tons in 60 days would yield a profit of £145 16s. 8d. over and above the 10 per cent interest on the investment. A yield of 10 tons of tunas, if sold at 7½d. per 100lb., would bring in £6 5s. per acre, which is considered to be a good return for otherwise worthless land, and entailing little or no cultivation.

## New Patents.

THIS List is specially compiled for the *Chemical News* by Messrs Rayner & Co , Registered Patent Agents, of 5, Chancery Lane, London, W C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously

*Latest Patent Applications.*

22885—British Thomson Houston Co.—Chemical apparatus. August 29.
23286—Cassela & Co —Manufacture of salts of acridinium compounds. September 1.
23354—Steinhilber, H.—Process for producing cellulose, from cyperacaes, graminaes and typhacaes. September 2.

*Specifications published this Week.*

136564—Hansgirg, F —Method of obtaining perylene.
145085—Mond, A L.—Process for treating salamoniac skimmings.
157971—Wallin, E.—Method of treating a stonelike material including wood saw-dust from magnesium and magnesium salts

*Abstracts Published this Week.*

*Ammonium Sulphate.*—Patent No. 166036.—Mr. G P. Heisch, of Brentford Gas Co., Southall, Middlesex, has designed and patented

FIG.I.

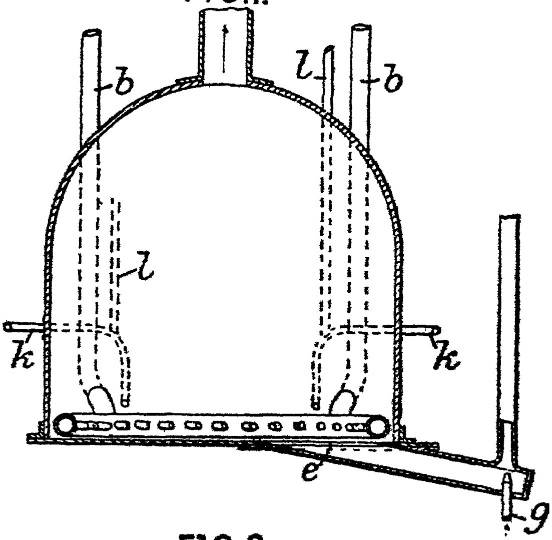
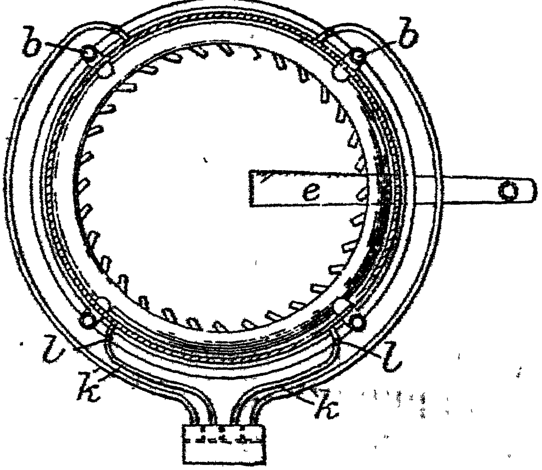



FIG.2.



an improved ammonium sulphate saturator, which is illustrated in accompanying drawing. It is constructed with a flat bottom and contains no pipes or apparatus except means for introducing the ammoniacal gases. The latter enter through a number of jets which discharge tangentially, and in the same direction from a circular feed-pipe. The ammonium sulphate crystals collect in the vortex which is produced and are withdrawn by means of a pipe leading from the middle, of the bottom of the saturator to an ejector situated outside. In the apparatus shown, ammonia is introduced through the pipes *b*, and acid through the pipes *k*, which are provided with vents *l*, to enable gas generated in the pipes, or air sucked in with the acid, to escape. The ammonium sulphate passes down the slot *e* to the ejector *g*.

*Amino Compound.*—Patent No. 166283.—Mr. D. A. Legg, of 17, Pepys Road, Raynes Park, and M. A. Adam, of 57, Lincoln's Inn Fields, London, have patented an improved process for the preparation of Amino Compounds. They are prepared by passing nitro compounds such as nitrobenzene snd nitrotoluene, in the vapour phase and together with hydrogen, water gas, etc., over or in contact with the copper catalyst described in Specificati n 166,249; or in the place of hydrogen as such, there may be employed a body such as secondary butyl alcohol, which is capable of being dehydrogenated under the conditions suitable for the reduction of the nitro compounds, in which case there is obtained in addition to the amino compound, methyl ethyl ketone, or if methyl alcohol is employed the reaction product of formaldehyde and aniline. The catalyst is revivified by heating in air to temperatures between 300 and 1000° C.

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# BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

EDINBURGH, 1921.

## PROBLEMS OF PHYSICS.

ADDRESS DELIVERED BEFORE SECTION A (MATHEMATICS AND PHYSICS)

By PROFESSOR O. W. RICHARDSON, D.Sc., F.R.S., President of the Section.

MY predecessor in office a year ago reminded you that the theoretical researches of Einstein and Weyl suggest that not merely the material universe, but space itself is finite. As to the probabilities, I do not wish to express an opinion; but the statement is significant of the extent of the revolution in the conceptions and fundamental principles of physics now in progress. That space need not be infinite has, I believe, long been recognised by geometricians, and appropriate geometries to meet its possible limitations have been devised by ingenious mathematicians. I doubt, however, whether these inventive gentlemen ever dreamed that their schemes held any objective validity such as would assist the astronomer and the physicist in understanding and classifying material phenomena. It is not certain that they will; but the possibility is definite. Apart from this, the whole development of relativity is an extraordinary triumph for pure mathematics. Had Einstein not found his entire calculus ready to hand, owing to the purely mathematical work of Christoffel, Riemann, and others, it seems certain that the development of generalised relativity would have been much slower. It is a pleasure to be able to acknowledge this indebtedness of physics and astronomy to pure mathematics.

Relativity is the revolutionary movement in physics which has caught the public eye, perhaps because it deals with familiar conceptions in a manner which for the most part is found pleasantly incomprehensible. But it is only one of a number of revolutionary changes of comparable magnitude. Among these we have to place the advent of the quantum, the significance of which I hope we shall thoroughly discuss early next week. The various consequences of the electronic structure of matter are still unfolding themselves to us, and are increasing our insight into the most varied phenomena at a rate which must have appeared incredible only a few decades ago.

The enormous and far-reaching importance of the discoveries being made at Cambridge by Sir Ernest Rutherford cannot be over-emphasised. These epoch-making discoveries relate to the structure and properties of the nuclei of atoms. At the present time we have, I think, to accept it as a fact that the atoms consist of a positively charged nucleus of minute size, surrounded at a fairly respectful distance by the number of electrons requisite to maintain the structure electrically neutral. The nucleus contains all but about one-two-thousandth part of the mass of the atom, and its electric charge is numerically equal to that of the negative electron multiplied by what is called the atomic number of the atom, the atomic number being the number which is obtained when the chemical elements are enumerated in the order of the atomic weights; thus hydrogen=1, helium=2, lithium=3, and so on. Consequently the number of external electrons in the atom is also equal to the atomic number. The evidence, derived from many distinct and dissimilar lines of enquiry, which makes it necessary to accept the foregoing statements as facts, will be familiar to members of this Section of the British Association, which has continually been in the forefront of contemporary advances in physical science. But I would remind you in passing that one of the important pieces of evidence was supplied by Prof. Barkla's researches on the scattering of X-rays by light atoms.

The diameters of the nuclei of the atoms are comparable with one-millionth of one-millionth part of a centimetre, and the problem of finding what lies within the interior of such structure seems at first sight almost hopeless. It is to this problem which Rutherford has addressed himself by the direct method of bombarding the nuclei of the different atoms with the equally minute high-velocity helium nuclei (alpha-particles) given off by radioactive substances, and examining the tracks of any other particles which may be generated as a result of the impact. A careful and critical examination of the results shows that hydrogen nuclei are thus expelled from the nuclei of a number of atoms such as nitrogen and phosphorus. On the other hand, oxygen and carbon do not eject hydrogen under these circumstances, although there is evidence in the case of oxygen and nitrogen of the expulsion of other sub-nuclei whose precise structure is a matter for further inquiry.

The artificial transmutation of the chemical elements is thus an established fact. The natural transmutation has, of course, been familiar for some years to students of radioactivity. The philosopher's stone, one of the alleged chimeras of the mediæval alchemists, is thus within our reach. But this is only part of the story. It appears that in some cases the kinetic energy of the ejected fragments is greater than that of the bombarding particles. This means that these bombardmens are able to release the energy which is stored in the nuclei of atoms. Now, we know from the amount of heat liberated in radioactive disintegration that the amount of energy stored in the nuclei is of a higher order of magnitude altogether, some millions of times greater, in fact, than that generated by any chemical reaction such as the combustion of coal. In this comparison, of course, it is the amount of energy per unit mass of reacting or disintegrating matter which is under consideration. The amounts of energy which have thus far been released by artificial disintegration of the nuclei are in themselves small, but they are enormous in comparison with the minute amounts of matter affected. If these effects can be sufficiently intensified, there appear to be two possibilities. Either they will prove

uncontrollable, which would presumably spell the end of all things, or they will not. (To reassure the nervous I would, however, interpolate the comforting thought that this planet has held considerable quantities of radioactive matter for a very long time without anything very serious happening so far as we know.) If they can be both intensified and controlled, then we shall have at our disposal an almost illimitable supply of power which will entirely transcend anything hitherto known. It is too early yet to say whether the necessary conditions are capable of being realised in practice, but I see no elements in the problem which would justify us in denying the possibility of this. It may be that we are at the beginning of a new age, which will be referred to as the age of sub-atomic power. We cannot say; time alone will tell.

*Thermionic Emission.*

With your permission, I will now descend a little way from the summit of Mount Olympus, and devote the rest of my address to a sober review of the present state of some of the questions with which my own thoughts have been more particularly occupied. At the Manchester meeting of the Association in 1915, I had the privilege of opening a discussion on thermionic emission—that is to say, the emission of electrons and ions by incandescent bodies. I recall that the opinion was expressed by some of the speakers that these phenomena had a chemical origin. That view, I venture to think, is one which would find very few supporters now. It is not that any new body of fact has arisen in the meantime. The important facts were all established before that time, but they were insufficiently appreciated, and their decisiveness was inadequately realised.

It may be worth while to revert for a moment to the issues in that controversy, already moribund in 1915, because it has been closely paralleled by similar controversies relating to two other groups of phenomena—namely, photoelectric emission and contact electromotive force—which, as we shall see, are intimately connected with thermionic emission. The issue was not as to whether thermionic emission may be looked upon simply as a type of chemical reaction. Such an issue would have been largely a matter of nomenclature. Thermionic electron emission has many features in common with a typical reversible chemical reaction such as the dissociation of calcium carbonate into lime and carbon dioxide. There is a good deal to be said for the point of view which regards thermionic emission as an example of the simplest kind of reversible chemical action, namely, that kind which consists in the dissociation of a neutral atom into a positive residue and a negative electron, inasmuch as we know that the negative electron is one of the really fundamental elements out of which matter is built up. The issue in debate was, however, of a different character. It was suggested that the phenomenon was not primarily an emission of electrons from the metallic or other source, but was a secondary phenomenon, a kind of by-product of an action which was primarily a chemical reaction between the source of electrons and some other material substance such as the highly attenuated gaseous atmosphere which surrounded it. This suggestion carried with it either implicitly or explicitly the view that the source of power behind the emission was not the thermal energy of the source, but was the chemical energy of the postulated reactions.

This type of view has never had any success in elucidating the phenomena, and I do not feel it necessary at this date to weary you with a recital of the facts which run entirely counter to it, and, in fact, definitely exclude it as a possibility They have been set forth at length elsewhere on more than one occasion. I shall take it to be established that the phenomenon is physical in its origin and reversible in its operation.

Establishing the primary character of the phenomenon does not, however, determine its nature or its immediate cause. Originally I regarded it as simply kinetic, a manifestation of the fact that as the temperature rose the kinetic energy of some of the electrons would begin to exceed the work of the forces by which they are attracted to the parent substance. With this statement, there is, I think, no room for anyone to quarrel, but it is permissible to inquire how the escaping electrons obtain the necessary energy. One answer is that the electrons have it already in the interior of the substance by virtue of their energy of thermal agitation. But thermal agitations now appear less simple than they used to be regarded, and in any event they do not exhaust the possibilities.

We know that when light of short enough wavelength falls on matter it causes the ejection of electrons from it—the so-called photo-electric effect. Since the formula for the radiation emitted by a body at any given temperature contains every wave-length without limitation, there must be some emission of electrons from an incandescent body as the result of the photoelectric effect of its own luminosity. Two questions obviously put themselves. Will this photoelectric emission caused by the whole spectrum of the hot body vary as the temperature of the incandescent body is raised in the way which is known to characterise thermionic emission? A straightforward thermodynamic caluculation shows that this is to be expected from the theoretical standpoint, and the anticipation has been confirmed by the experiments of Prof. W. Wilson. Thus the autophotoelectric emission has the correct behaviour to account for the thermionic emission. The other question is: Is it large enough? This is a question of fact. I have considered the data very carefully. There is a little uncertainty in some of the items, but when every allowance is made there seems no escape from the conclusion that the photoelectric effect of the whole spectrum is far too small to account for thermionic emission.

This question is an important one, apart from the particular case of thermionic emission. The same dilemma is met with when we seek for the actual *modus operandi* of evaporation, chemical action, and a number of other phenomena. These, so far as we know, might be fundamentally either kinetic or photochemical or a mixture of both. In my judgment the last alternative is the most probable. (I am using the term photochemical here in the wide sense of an effect of light in changing the composition of matter, whether the parts affected are atoms, groups of atoms, ions, or electrons.) For example, the approximation about boiling points known as Trouton's rule is a fairly

obvious deduction from the photochemical standpoint. The photochemical point of view has recently been put very strongly by Perrin, who would make it the entire *motif* of all chemical reaction, as well as of radioactivity and changes of state. In view of the rather minor part it seems to play in thermionic emission, where one would *a priori* have expected light to be especially effective, this is probably claiming too much for it, but the chemical evidence contains one item which is certainly difficult to comprehend from the kinetic standpoint The speed of chemical decomposition of certain gases is independent of their volume, showing that the decomposition is not due to molecular collisions. The speed does, however, increase very rapidly with rising temperature What the increased temperature can do except increase the number and intensity of the collisions, factors which the independence of volume at constant temperature show to be without effect, and increase the amount of radiation received by the molecules, is not too obvious It seems, however, that, according to calculations by Langmuir (*Journ. Am. Chem. Soc.*, 1920, xlii., 2190), the radiation theory does not get us out of this difficulty; for, just as in the ordinary photoelectric case, there is nothing like enough radiation to account for the observed effects. It seems that in the case of these mono-molecular reactions the phenomena cannot be accounted for either by simple collisions, or by radiation, or by a mixture of both, and it is necessary to fall back on the internal structure of the decomposing molecule. This is complex enough to afford material sufficient to cover the possibilities; but, from the standpoint of the temperature energy relations of its parts, it cannot at present be regarded as much more than a field for speculation.

*Contact Electricity.*

A controversy about the nature of the contact potential difference between two metals, similar to that to which I have referred in connection with thermionic emission, has existed for over a century. In 1792 Volta wrote: "The metals . . . can by themselves, and of their own proper virtue, excite and dislodge the electric fluid from its state of rest." The contrary position that the electrical manifestations are inseparably connected with chemical action was developed a few years later by Fabroni. Since that time electrical investigators have been fairly evenly divided between these two opposing camps. Among the supporters of the intrinsic or contact view of the type of Volta, we may recall Davy, Helmholtz, and Kelvin. On the other side we have to place Maxwell, Lodge, and Ostwald. In 1862 we find Lord Kelvin ("Papers on Electrostatics and Magnetism," p. 318) writing: "For nearly two years I have felt quite sure that the proper explanation of voltaic action in the common voltaic arrangement is very near Volta's, which fell into discredit because Volta or his followers neglected the principle of the conservation of force." On the other hand, in 1896, we find Ostwald (*Elektochemie, Ihre Geschichte und Lehre*, Leipzig, 1896, p. 65), referring to Volta's views as the origin of the most far-reaching error in electrochemistry, which the greatest part of the scientific work in that domain has been occupied in fighting almost ever since. These are cited merely as representative specimens of the opinions of the protagonists.

Now, there is a close connection between thermionic emission and contact potential difference, and I believe that a study of thermionic emission is going to settle this little dispute. In fact, I rather think it has already settled it, but before going into that matter I would like to explain how it is that there is a connection between thermionic emission and contact potential difference, and what the nature of that connection is.

Imagine a vacuous enclosure, either impervious to heat or maintained at a constant temperature. Let the enclosure contain two different electron-emitting bodies, A and B. Let one of these, say A, have the power of emitting electrons faster than the other, B. Since they are each receiving as well as emitting electrons, A will acquire a positive and B a negative charge under these circumstances. Owing to these opposite charges, A and B will now attract each other, and useful work can be obtained by letting them come in contact. After the charges on A and B have been discharged by bringing them in contact, let the bodies be quickly separated and moved to their original positions. This need involve no expenditure of work, as the charges arising from the electron emission will not have had time to develop. After the charges have had time to develop the bodies can again be permitted to move together under their mutual attraction, and so the cycle can be continued an indefinite number of times. In this way we have succeeded in imagining a device which will convert all the heat energy from a source at a uniform temperature into useful work.

Now, the existence of such a device would contravene the second law of thermodynamics. We are, therefore, compelled either to deny the principles of thermodynamics or to admit that there is some fallacy as to the pretended facts in the foregoing argument. We do not need to hesitate between these alternatives, and we need only look to see how the alleged behaviour of A and B will need to be modified in order that no useful work may appear. There are two alternatives. Either A and B necessarily emit equal numbers (which may include the particular value zero) of electrons at all temperatures, or the charges which develop owing to the unequal rate of emission are not discharged, even to the slightest degree, when the two bodies are placed in contact.

The first alternative is definitely excluded by the experimental evidence, so I shall proceed to interpret the second. It means that bodies have natural states of electrification whereby they become charged to definite potential differences whose magnitudes are independent of their relative positions. There is an intrinsic potential difference between A and B which is the same, at a given temperature, whether they are at a distance apart or in contact. In the words of Volta, which I have already quoted, "the metals can by themselves, and of their own proper virtue, excite and dislodge the electric fluid from its state of rest."

Admitting that the intrinsic potentials exist, a straightforward calculation shows that they are intimately connected with the magnitudes of the thermionic emission at a given temperature. The relation, is, in fact, governed by the following equation: If A and B denote the saturation thermionic currents per unit area of the bodies A and

B respectively, and V is the contact potential difference between them at the absolute temperature T, then $V = \frac{kT}{e} \log \frac{A}{B}$ where $k$ is the gas constant calculated for a single molecule (Boltzmann's constant), and $e$ is the electronic charge.

I have recently, with the help of Mr. F. S. Robertson, obtained a good deal of new information on this question from the experimental side. We have made measurements of the contact potential difference between heated filaments and a surrounding metallic cylinder, both under the high-vacuum and gas-free conditions which are now attainable in such apparatus, and also when small known pressures of pure hydrogen are present. As is well kown, both contact potentials and thermionic emission are very susceptible to minute traces of gas, but we find that under the best conditions as to freedom from gas there is a contact potential of the order of one volt between a pure tungsten filament and a thoriated filament. We have also been able to measure the thermionic emissions from the filaments at the same time, and we find that the contact potential calculated from them with the help of the foregoing equation is within 20 per cent of the measured value. Considering the experimental difficulties, this is a very substantial agreement. Whilst the evidence is not yet as complete as I hope to make it, it goes a long way towards disproving the chemical view of the orign of contact potential difference.

From what has been said you will realise that the connection between contact potentials and thermionic emissions is a very close one. I would, however, like to spend a moment in developing it from another angle. To account for the facts of thermionic emission it is necessary to assume that the potential energy of an electron in the the space just outside the emitter is greater than that inside by a definite amount, which we may call $w$. The existence of this $w$, which measures the work done when an electron escapes from the emitter, is required by the electron-atomic structure of matter and of electricity. Its value can be deduced from the temperature variation of thermionic emission, and, more directly, from the latent heats absorbed or generated when electrons flow out of or into matter. These three methods give values of $w$ which, allowing for the somewhat considerable experimental difficulties, are in fair agreement for any particular emitter. The data also show that in general different substances have different values of $w$. This being so, it is clear that when uncharged bodies are placed in contact the potential energies of the electrons in one will in general be different from those of the electrons in the other. If, as in the case of the metals, the electrons are able to move freely, they will so move until an electric field is set up which equilibrates this difference of potential energy. There will thus be an intrinsic or contact difference of potential between metals which is equivato the difference in the values of $w$ and is equal to the difference in $w$ divided by the electronic charge. (This statement is only approximately true. In order to condense the argument, certain small effects connected with the Peltier effect at the junction between the metals have been left out of consideration).

*Photoelectric Action.*

We have seen that there is a connection on broad lines between thermionic emission and both contact potentials on the one hand, and photoelectric emission on the other. The three groups of phenomena are also related in detail and to an extent which up to the present has not been completely explored. In order to understand the present position, let us review briefly some of the laws of photoelectric action as they have revealed themselves by experiments on the electrons emitted from metals when illuminated by visible and ultra-violet light.

Perhaps the most striking feature of photoelectric action is the existence of what has been called the threshold frequency. For each metal whose surface is in a definite state there is a definite frequency $n_0$, which may be said to determine the entire photoelectric behaviour of the metal. The basic property of the threshold frequency $n_0$ is this: When the metal is illuminated by light of frequency less than $n_0$ no electrons are emitted, no matter how intense the light may be. On the other hand, illumination by the most feeble light of frequency greater than $n_0$ causes some emission. The frequency $n_0$ signalises a sharp and absolute discontinuity in the phenomena.

Now let us inquire as to the kinetic energy of the electrons which are emitted by a metal when illuminated by monochromatic light of frequency, let us say, $n$. Owing to the fact that the emitted electrons may originate from different depths in the metal, and may undergo collisions at irregular intervals, it is only the maximum kinetic energy of those which escape which we should expect to exhibit simple properties. As a matter of fact, it is found that the maximum kinetic energy is equal to the difference between the actual frequency $n$ and the threshold frequency $n_0$ multiplied by Planck's constant $h$. In mathematical symbols, if $v$ is the velocity of the fastest emitted electron, $m$ its mass, $e$ its charge, and V the opposing potential required to bring it to rest,

$$eV = \tfrac{1}{2}mv^2 = h(n - n_0).$$

From this equation we see that the threshold frequency has another property. It is evidently that frequency for which kinetic energy and stopping potential fall to zero. This suggests strongly, I think, that the reason the electron emission ceases at $n_0$ is that the electrons are not able to get enough energy from the light to escape from the metal, and not that they are unable to get any energy from the light.

The threshold frequencies have another simple property. If we measure the threshold frequencies for any pair of metals, and at the same time we measure the contact difference of potential K between them, we find that K is equal to the difference between their threshold frequencies multiplied by this same constant $h$ divided by the electronic charge $e$.

These results, as well as others which I have not time to enumerate, admit of a very simple interpretation if we assume that when illuminated by light of frequency $n$ the electrons individually acquire an amount of energy $hn$. We have seen that in order to account for thermionic phenomena it is necessary to assume that the electrons have to do a certain amount of work $w$ to get away from the emitter. There is no reason to suppose

that photoelectrically emitted electrons can avoid this necessity. Let us suppose that his work is also definite for the photoelectric electrons and let us denote its value by $hn_0$. Then no electron will be able to escape from the metal until it is able to acquire an amount of energy at least equal to $hn_0$ from the light—that is to say, under the suppositions made—until $n$ becomes at least as great as $n_0$. Thus $n_0$ will be identical with the frequency which we have called the threshold frequency, and the maximum energy of any electron after escaping will be $h\ (n-n_0)$

The relation between threshold frequencies and contact potential difference raises another issue. We have seen that the contact potential difference beween two metals must be very nearly equal to the difference between the amounts of work $w$ for the electrons to get away from the two metals by thermionic action, divided by the electronic charge $e$. The photoelectric experiments show that the contact electromotive force is also nearly equal to the differences of the threshold frequencies multiplied by $h/e$. It follows that the photoelectric work $hn_0$ must be equal to the thermionic work $w$ to the same degree of accuracy. We have to except here a possible constant difference between the two. I do not see, however, how any value other than zero for such a constant could be given a rational interpretation, as it would have to be the same for all substances and frequencies. The photoelectric and thermionic works are known to agree to within about one volt. To decide how far they are identical needs better experimental evidence than we have at present. The indirect evidence for their substantial identity (that is to say, within the limits of accuracy referred to above) is stronger at the moment than the direct evidence.

I do not think that the complete identity of the thermionic work $w$ and the photoelectric $hn_0$ is a matter which can be inferred *a priori*. What we should expect depends to a considerable extent on the condition of the electrons in the interior of metals. We cannot pretend to any real knowledge of this at the present; the various current theories are mere guesswork. Unless the electrons which escape all have the same energy when inside the metal we should expect the thermionic value to be an average taken over those which get out. The photoelectric value, on the other hand, should be the minimum pertaining to those internal electrons which have most energy. The apparent sharpness of the threshold frequency is also surprising from some points of view. There seems to be scope for a fuller experimental examination of these questions.

I have spoken of the threshold frequency as though it were a perfectly definite quantity. No doubt it is when the condition of the body is or can be definitely specified, but it is extraordinarily sensitive to minute changes in the conditions of the surface, such as may be caused, for example, by the presence of extremely attenuated films of foreign matter. For this reason we should accept with a certain degree of reserve statements which appear from time to time that photoelectric action is some parasitic phenomenon, inasmuch as it can be made to disappear by improvement of vacuum, or other change in the conditions. What has generally happened in these investigations is, that something has been done to the illuminated surface which has raised its threshold frequency above that of the shortest wave-length in the light employed in the test. Unless they are accompanied by specific information about the changes which have taken place in the threshold frequency, such statements are of little value at the present stage of development of this subject.

Interesting calculations have been made by Frenkel which bring surface tension into close connection with the thermionic work $w$. Broadly speaking, there can be little doubt that a connection of this nature exists, but whether the relation is as simple as that given by the calculations is open to doubt. It should be possible to answer this question definitely when we have more precise information about the disposition of the electrons in atoms such as the continuous progress in X-ray investigation seems to promise.

*Light and X-Rays.*

One of the great achievements of experimental physics in recent years has been the demonstration of the essential unity of X-rays and ordinary light. X-rays have been shown to be merely light of particularly high frequency or short wavelength, the distinction between the two being one of degree rather than of kind. The foundations of our knowledge of X-ray phenomena were laid by Barkla, but the discovery and development of the crystal diffraction methods by v. Laue, the Braggs, Mosley, Duane, and de Broglie have established their relations with ordinary light so clearly that he who runs may read their substantial identity. The actual gap in the spectrum of the known radiations between light and X-rays is also rapidly disappearing. The longest stride into the region beyond the ultra-violet was made by Lyman with the vacuum grating spectroscope which he developed. For a short time Prof. Bazzoni and I held the record in this direction with our determination of the short wave limit of the helium spectrum, which is in the neighbourhood of 450 Ångstrom units. More recently this has been passed by Millikan, who has mapped a number of lines extending to about 200 Ångstrom units—that is to say, more than four octaves above the violet limit of the visible spectrum. I am not sure what is the longest X-ray which has been measured, but I find a record of a Zinc L-ray by Friman (*Phil. Mag.*, 1916, xxxii., 494) of a wavelength of 12·346 Ångstrom units. There is thus at most a matter of about four octaves still to be explored. In approaching this unknown region from the violet end, the most characteristic property of the radiaitons appears to be their intense absorption by practically every kind of matter. This result is not very surprising from the quantum standpoint. The quantum of these radiations is in excess of that which corresponds to the ionising potential of every known molecule, but it is of the same order of magnitude. Furthermore, it is large enough to reach not only the most superficial, but also a number of the deeper-seated electrons of the atoms. There is evidence, both theoretical and experimental, that the photoelectric absorption of radiation is most intense when its quantum exceeds the minimum quantum necessary to eject the absorbing electron but does not exceed it too much. In the simplest theoretical case the absorption is zero for radiations whose frequencies lie below the minimum quantum, rises

to a maximum for a frequency comparable with the minimum, and falls off to zero again at infinite frequency. This case has not been realised in practice, but, broadly judged, the experimental data are in harmony with it. On these general grounds we should expect intense absorption by all kinds of matter for the radiation between the ultra-violet and the X-ray region.

The closeness of the similarity in the properties of X-rays and light is, I think, even yet inadequately realised. It is not merely a similarity along broad lines, but it extends to a remarkable degree of detail. It is perhaps most conspicuous in the domains of photoelectric action and of the inverse phenomenon of the excitation of radiation or spectral lines by electron impacts. Whilst there may still be room for doubt as to the precise interpretation of some of the experimental data, the impression I have formed is that each important advance tends to unify rather than to disintegrate these two important groups of phenomena.

## THE STRUCTURAL RELATION OF ISOQUINOLINE AND PHENANTHRENE ALKALOIDS.

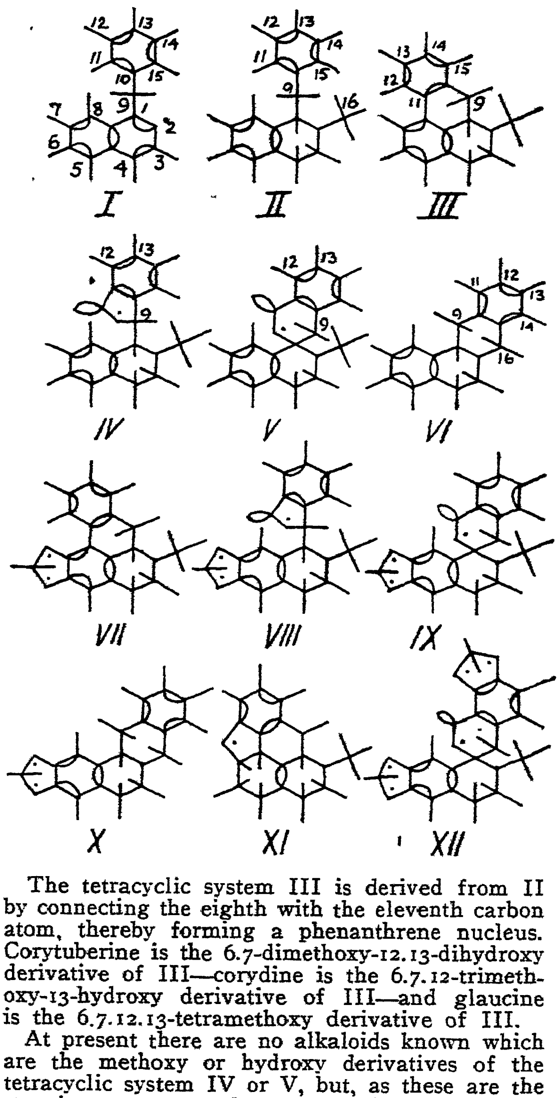
By INGO W. D. HACKH.

An interesting structural relation among alkaloids containing the isoquinoline nucleus was revealed by working with their structure symbols (*Canadian Chem. Journ.*, 1918, ii., 135; *Science*, 1918, xlviii., 333; *Chem. Eng.*, 1918, xxvi., 377; Chemical News, cxviii., 289, and cxxi., 85; *Chem. Age* (London), iii., 392; *Journ. Am. Pharm. Assoc.*, 1920, ix., 392). Comparing the structural formulas of morphine (Pschorr), berberine (Parkin), papaverine (Goldschmidt), glaucine (Fischer), narcotine (Perkin and Robinson), corydaline (Dobbie and Lauder), dicentrine (Gadamer), protopine and cryptopine (Perkin), &c., as usually given in chemical literature will not indicate any relationship in structure, in fact, these alkaloids appear to belong to entirely different groups. If these structural formulas, or the corresponding structure symbols, however, are turned and shifted so as to bring the isoquinoline nucleus into the same relative position; it is possible to trace a structural relationship which genetically connects all these alkaloids.

Thus the unsaturated tricyclic system I or 1-benzyl-isoquinoline may be used as the starting-point for the structural derivation of a great number of alkaloids. Paperoline is the 6.7.12.13-tetrahydroxy derivative of I, and papaverine is the 6.7.12.13-tetramethhoxy derivative of I.

By partial saturation and methylation the ring-system II or 1.3.4-trihydro-N-Methyl-1-benzyl-iso quinoline is derived. This is the parent compound of laudanosine which is the 6.7.12.13-tetramethoxy derivative of II.

The hydrocarbon II contains a benzene and isoquinoline nucleus, and is thus a tricyclic system from which in four different ways an additional ring formation tetracyclic systems are derived; each of them characteristic of certain alkaloids. Thus the fourth ring can be formed by direct connection of the eights with the eleventh carbon atom (III), by a lactone formation between the ninth and eleventh carbon atom (IV) giving a pentatomic ring, by lactone formation between the first and eleventh carbon atom (V) giving a hexatomic ring, or finally by connecting the fifteenth carbon atom with the N-methyl carbon atom (VI).




The tetracyclic system III is derived from II by connecting the eighth with the eleventh carbon atom, thereby forming a phenanthrene nucleus. Corytuberine is the 6.7-dimethoxy-12.13-dihydroxy derivative of III—corydine is the 6.7.12-trimethoxy-13-hydroxy derivative of III—and glaucine is the 6.7.12.13-tetramethoxy derivative of III.

At present there are no alkaloids known which are the methoxy or hydroxy derivatives of the tetracyclic system IV or V, but, as these are the stepping stones to the pentacyclic system VIII and IX, and the hexacyclic system XII, it appears that their existence is possible and the prediction of their occurrence in plants is plausible.

The tetracyclic system VI is derived from II by connecting the N-methyl carbon atom with the fifteenth carbon atom. Corydaline is the 9-methyl-12.13-dimethoxy derivative of VI.

From the four tetracyclic systems, III, IV, V, and VI, there are five pentacyclic systems derived by the formation of an additional penatomic ring which is usually produced by attaching a methylene dioxy group ($-O.CH_2-O-$) to the sixth and seventh carbon atoms. The relation of these systems is shown by the diagram:

Tricyclic: II

Tetracyclic: III IV V VI

Pentacyclic: XI VII VIII IX X

Hexacyclic: XII

The pentacyclic system VII has the methylene-dioxy group in the 6.7-position, and its 12.13-dimethoxy derivative is dicentrine—the 12-hydoxy-13-methoxy derivative is bulbocapnine.

The pentacyclic system VIII is represented in hydrastine, the 12.13-dimethoxy derivative, and narcotine, the 8.12.13-trimethoxy derivative. Cryptopine is the compound given in IX, and berberine is the 9-hydroxy-12.13-dimethoxy derivative of X.

The fifth pentatomic ring may also be formed by connecting the seventh and twelfth carbon atom of III by an oxygen atom, thus the pentacyclic system XI results. If partially saturated, this forms the parent compound of the morphine alkaloids. Thus morphine is the 6.13-dihydroxy derivative of XI, codeine the 6-hydroxy-13-methoxy derivative, dionine the 6-hydroxy-13-ethoxy derivative, and thebaine the 6.13-dimethoxy derivative of XI.

Only one instance is on record in which the structure of an isoquinoline alkaloid contains six rings, as shown in XII for protopine. This hexacyclic system is derived from IX by attaching the second methylene dioxy group to the twelfth and thirteenth carbon atom.

It is of interest to note that substitution practically always takes place at the 6.7- and 12.13-position, whether it be by the hydroxy, methoxy, ethoxy, or the methylene-dioxy group. It is also significant to note that the apparent genetic relation among these alkaloids, although the respective structural formulas have been determined at different times by different investigators. In this connection it appears likewise that the morphine formula, as given by Pschorr, is the correct one, and more plausible than those given by Freund and others. These structural relations enable the following classification of the alkaloids:

Laudanosine
Papaverine
Paperoline, &c.

Corydine
Corytuberine
Glaucine, &c.

?

?

Corydaline, &c.

Morphine
Codeine
Dionine
Thebaine, &c.

Dicentrine
Bulbocapnine, &c

Hydrastine
Narcotine, &c.

Cryptopine, &c.

Protopine, &c.

Berberine
Canadine
Artarine, &c.

San Francisco, Cal,
College of Physicians and Surgeons.

## THE ELECTRIC FURNACE SPECTRUM OF SCANDIUM.*

By ARTHUR S. KING.

SCANDIUM occurs in small amounts in a number of the rare-earth minerals, but its extraction in a fair degree of purity is an exceedingly difficult matter, and, as its separation has not been stimullated by any commercial application, the substance is extremely scarce. The late Sir William Crooks (*Philosophical Transactions*, A, 1909, ccix., 15) described his examination of a large number of minerals in a search for those containing scandium. Wiikite, found in Finland, proved to contain over 1 per cent of scandium oxide (scandia), and was used by him to furnish pure scandia. The final difficulty in the tedious process of separation was the elimination of the closely related elements yttrium and ytterbium.

The spectrum of scandium is especially interesting on account of the peculiar intensity relations, to be discussed presently, among the scandium lines in the solar spectrum. An examination of the behaviour of the lines at various temperatures of the electric furnace was therefore desirable, in order to determine the part which temperature may play in bringing about the peculiarities observed.

Through the good offices of Prof. Fowler, I have been able recently to obtain a sufficient amount of highly purified scandia to carry out the examination of the furnace spectrum. This scandia was prepared by Sir William Crookes. His former assistant, Mr. J. H. Gardiner, very kindly placed the material at my disposal through Prof. Fowler.

In the earlier solar investigations in which the spot spectrum was studied, it was noted that certain lines intensified in the spot coincided with lines in the scandium arc, while other strong arc lines were absent in the spot though present in the solar spectrum and prominent in the chromosphere. Fowler (*ibid.*, A., 1909, ccix., 47) explained this phenomenon by producing, besides

* Abridgement of a Paper on the Electric Furnace Spectrum of Scandium. Contribution from the Mount Wilson Observatory, No. 211.

he regular arc spectrum, the spectrum of the arc n hydrogen, which approaches that of the spark, and the spectrum of the flame of the arc, in which ertain lines are given a high intensity. His results showed clearly that the lines prominent in he spot spectrum are those given by the flame of he arc, and probably result from a reduced temperature in the spot, while the scandium lines missing from the spot spectrum are enhanced ines, though present often with considerable intensity in the arc. The occurrence of three distinct types, enhanced, arc, and flame lines, in the scandium arc is a feature shown by some other elements, notably titanium, the low-temperature ines of which have been selected by the furnace *Mt. Wilson Contr.*, No. 76; *Astrophys. Journ.*, 1914, xxxix, 139), while many lines prominent in the arc are much enhanced in the spark.

*Experimental Method.*

The tube-resistance furnace was operated as usual, the chamber being pumped out to a few millimetres' pressure. To avoid scattering of the scandia in the tube, the powder was put in a small combustion boat of graphite, which was placed at the middle of the furnace-tube. The image of the space above this boat was focused on the slit of the spectrograph. The scandia fused in the boat, entering to some extent into the graphite as if a carbide were formed. The fused residue was a shining black when removed from the tube, but after exposure to the air for some time turned to a grey-brown powder, presumably from the reabsorption of oxygen.

The spectrograms were made with a 15ft. concave grating spectrograph, the second order with a dispersion of 1 mm. = 1·86 A being used for the ultra-violet, and the first order for the region from $\lambda$3800 into the red.

*Conclusion.*

The varying response of spectrum lines to temperature change, observed in the study at different temperatures of the furnace spectrum of scandium, has concerned itself especially with the conditions of appearance and development of the three main types—enhanced, arc, and low-temperature lines—which make up the spectrum. The scandium enhanced lines, as regards degree of excitation required, stand between the enhanced lines of titanium and those of the type of H and K of calcium. For the lines appearing in the arc spectrum the regular temperature classification is carried out. The group of arc lines given by the arc flame consists of prominent low-temperature lines, but, since many lines strong in the furnace are relatively weak in all parts of the arc, additional data on this type of line are supplied by the furnace spectrum.

The explanation advanced by Fowler as to the relative strength of the different types of scandium lines in the solar and sun-spot spectra is fully confirmed by their varying response to the furnace excitation. The strong low-temperature lines, faint or lacking in the disc, are distinctly brought out in the spot, and, especially in the red, show high sensitiveness to the magnetic field. A comparison of the Zeeman effect for scandium in the laboratory with that shown in spot spectra and a fuller listing of the scandium lines present in the sun are needed to give this element its due place among those on which solar studies are based.—*Astrophysical Journal*, July, 1921.

## PROCEEDINGS OF SOCIETIES.

### INSTITUTE OF METALS.

*Birmingham Meeting, September* 21-22, 1921.

*"The Properties of Some Nickel-Aluminium-Copper Alloys."* By Prof. A. A. Read, D.Met., Member (Cardiff), and R. H. Greaves, M.Sc., Member (Woolwich).

In some of the copper-rich nickel-aluminium-copper alloys the alpha solution will retain much more nickel and aluminium at 900° C. than at ordinary temperatures. Alloys typical of the region comprised between the limits of composition of the alpha solution at 900° and at ordinary temperatures have been examined. These alloys while relatively soft on quenching from 900°, are hardened by slow cooling from that temperature, or by reheating to lower temperatures. This change is the result of the appearance of a new constituent (probably a nickel-aluminium-copper solid solution), the separation of which is accompanied by changes in the density and electrical conductivity of the alloy in addition to its effect on tensile, hardness, notched bar, and other tests. The separation of this special constituent takes place somewhat slowly, so that chill-cast alloys and hot-rolled rods of small section consist almost wholly of the alpha constituent. The cold-rolled rod, obtained by hot-rolling, followed by a few passes in the cold, thus consists almost wholly of the alpha constituent. On annealing the cold-rolled alloys, softening proceeds very slowly up to 500°, at which temperature precipitation of the nickel-aluminium rich constituent begins to take place at an appreciable rate, with the result that with some compositions a progressive increase of hardness is obtained by holding the alloy at 500° C. If the separation is sufficient, this may more than counterbalance the previous softening, giving an alloy of high elastic limit and tensile strength, and good elongation (*e.g.*, a maximum load of over 50 tons per square inch, with an elongation of 20 per cent). The rate of cooling from a temperature above that at which the alpha solution begins to deposit the special constituent has a great influence on the mechanical properties of the heat-treated alloys. The hardest product is, however, obtained by reheating the quenched alloy for some time at 600° to 700° C. (say two hours at 600°, or half-an-hour at 700°). The alloys so treated generally give better properties than are obtained by any uniform rate of slow cooling (*e.g.*, yield point over 20 tons per square inch, maximum load over 40 tons per square inch, elongation about 15 to 25 per cent). The heat-treated alloys show considerable endurance under alternating stresses above their true fatigue limit, the determination of which involves a number of prolonged tests.

*"The Effect of Increasing Proportions of Lead upon the Properties of Admiralty Gun-metal, with an Appendix dealing with the Effect of Lead on Gun-metal containing Copper* 85 *per cent, Tin* 5 *per cent, Zinc* 10 *per cent."* By R. T. Rolfe, F.I.C., Member (Bedford).

The effects of lead upon Admiralty gun-metal has been studied by the production of synthetic

alloys containing gradually increasing proportions of lead up to 1·68 per cent, subject to control as regards compositions, casting temperatures, and general conditions. Sand and chill-castings were produced, while a duplicate set of determinations were made on re-melts of the original alloys, thus checking the results from these and affording information on the variations in composition and properties caused by re-melting. In sand-cast gun-metal, lead gradually increases the strength, ductility, and softness of the alloy up to about 1·5 per cent of lead, but above this proportion causes a decrease in all three. Maximum repeated-impact resistance is obtained with 1 per cent of lead, falling away when this figure is exceeded. Lead does not affect the soundness, and is microscopically readily detectable on either the plain, polished, or etched surfaces. In chill-cast gun-metal, these effects are rather marked. The effect on the hardness parallels that of the sand-cast metal, with a change-point at about 1·5 per cent of lead, but associated with a minimum rather than a maximum strength figure. Increasing lead proportionately decreases the ductility and also the impact-figure of the metal twice melted, that melted once giving more irregular results. Lead does not affect the soundness, and is microscopically readily detectable on the plain polished surface. The influence of lead on liquation, machinability, corrosion, and behaviour for bearing purposes is also discussed, and it is suggested that in sand-cast gun-metal, the proportion of lead permitted by the Admiralty specification might with advantage be increased from 0·5 to 1 per cent. An Appendix deals with the influence of increasing proportions of lead upon the properties of gun-metal containing copper 85 per cent, tin 5 per cent, zinc 10 per cent.

"*The Density of the Zinc-Copper Alloys.*" By T. G. Bamford, M.Sc., Member (Birmingham).

The density of alloys, the author points out, is important both from a theoretical and a practical standpoint. When the correct density is known, it is possible to determine whether casting conditions have been satisfactory. Hitherto no trustworthy determinations of the densities of the copper-zinc series have been available. The author, after reviewing earlier work, records experiments conducted with alloys made from pure metals, and cast in sand- and chill-moulds respectively. The results indicate that there is a contraction in volume (*i.e.*, increase of density) due to alloying with mixtures containing more than 25 per cent of copper; and that the density of the sand cast (or slowly cooled) alloys is generally less than is the case with the chill castings, but that at points where the liquidus and solidus coincide on the constitutional diagram, chill castings and sand castings give the same values. These results afford striking confirmation of the data published by Turner and Murray on the volume changes of the copper-zinc alloys. The expansion recorded by these observers with alloys containing less than 30 per cent of copper is confirmed, and is shown to be connected with a new form of porosity different from ordinary unsoundness.

"*The Extrusion Defect.*" By R. Genders, M.B.E., B.Met., Member (Woolwich).

Experiments have been carried out with the object of devising a method of extrusion which would avoid the formation of the defect (known by the misleading term "piping") which is commonly found in a certain proportion of centrally extruded rod made from brass and other non-ferrous alloys by the usual hot-extrusion process. The defect is tubular in the interior of the rod, and generally exists in the last portion (up to 25 or 30 per cent) extruded. When a defective rod is broken across, the core frequently breaks at a different point from the outer ring, and projects, and is sometimes quite loose. It has been shown that the defect consists of foreign matter, oxide, and dezincified brass, which constituted the skin of the original billet. Billets extruded to various stages and sectioned axially show the presence of the defect in the shape of a funnel (formed by the turning inwards of the billet skin, which cannot flow along the side of the receiver owing to friction and its lower temperature) by the fact of the ram, and its gradual flow towards the die. The defect can be largely overcome by the use of a ram smaller in diameter than the billet, which causes the outer layer of the billet to remain in the receiver as a thin cylinder, but the method would probably be too wasteful on a large scale. By inverting the process so that the die is pushed through the billet, the mode of flow is altered. There is no relative movement between the billet and receiver, and flow is confined to the region of the die. Experiments on a small scale, using 60-40 brass billets and extruding under conditions comparable with large scale work, have shown this method to be successful in avoiding the "extrusion defect," the skin of the billet being turned over and collected on the face of the die, none entering the aperture of the die until the extrusion is nearly complete, when it emerges on the outside of the rod. The power required is less than with the method at present in use. Rod produced by the method is completely sound. The method is in use in many places for the production of tubes and rod from soft metals, although the plant appears to have been so designed only with a view to mechanical efficiency without any appreciation of possible effect on the quality of the product, and has not so far, to the author's knowledge, been used for hot extrusion of copper alloys. The necessary modifications of the plant would probably be fully justified by the saving of the very large amount of metal which by the present method is extruded only to be ultimately scrapped.

"*The Use of the Scleroscope on Light Specimens of Metals.*" By F. S. Tritton, Member (Teddington).

Some experience in the use of the scleroscope for testing the hardness of small pieces of metal in the laboratory led the author to doubt whether the real hardness values of small samples were obtained, although the usual precautions were taken to support the specimens in an apparently rigid manner. The experiments were undertaken with the view of finding out whether errors existed when using the ordinary methods of support, and, if so, to find some method of support that would eliminate them. Errors were detected, and to reduce them the author selected two materials, respectively

pitch and glucose, for the purpose of supporting the specimens in the scleroscope. The use of pitch requires a special clamp, a new type of which is described. On the other hand, without the use of a clamp, a solution of glucose considerably stiffer than treacle was found to give excellent results, the specimens under test being simply attached by means of the glucose to a hard steel base. In this way there could be readily tested the hardness of specimens having not merely flat but curved surfaces—such as balls or rollers—provided that a recessed support be made to fit the specimens.

"*The Constitution and Age-Hardening of the Alloys of Aluminium with Magnesium and Silicon.*" By D. Hanson, D.Sc., Member, and Marie L. V. Gayler, M.Sc., Member (Teddington).

Constitution of the Alloys.—The constitution of a small portion of the ternary system, aluminium, magnesium, silicon, has been investigated, namely that containing up to 35 per cent magnesium and 11 per cent silicon. The results of thermal curves and microscopic examination prove that in these alloys, magnesium and silicon form a chemical compound having the formula $Mg_2Si$. This compound and aluminium form a eutectiferous binary system, having a eutectic containing 13 per cent of $Mg_2Si$, and melting at 590° C. Two ternary systems are formed with silicon and magnesium respectively. The aluminium—$Mg_2Si$—silicon system possesses a ternary eutectic that melts at 550° C.; the ternary eutectic of the aluminium—$Mg_2Si$—magnesium system melts at 450° C. The solubility of the compound $Mg_2Si$ in solid aluminium has been determined, and the results show that $Mg_2Si$ is more soluble at high than at low temperatures, 1·6 per cent MgSi being held in solution at 580° C., and little more than 0·5 per cent $Mg_2Si$ at 30° C. Excess of silicon has little effect on the solubility of $Mg_2Si$, but magnesium reduces the solubility at high temperatures. This difference in the solubility of $Mg_2Si$ in solid aluminium at high and low temperatures is the cause of the age-hardening property of these alloys.

Age-Hardening of the Alloys.—The alloys of this system, after quenching from high temperatures, are relatively soft, but gradually become harder; this age-hardening ceases after a few days. The age-hardening of a series of alloys containing increasing amounts of $Mg_2Si$ rises progressively until the limit of the solubility of $Mg_2Si$ in aluminium at the quenching temperature is reached, beyond which the total increase in hardness remains constant. Hence the increase in hardness produced during the ageing of the alloys is roughly proportional to the amount of $Mg_2Si$ retained in solution by quenching. Confirmation of this view is also obtained from experiments with alloys of aluminium and $Mg_2Si$ with magnesium or silicon.

"*The Electrolytic Etching of Metals.*" By F. Adcock, M.B.E., B.Sc., Member (Ipswich).

As the title implies, electrolytic methods of etching various metals are described with a view to the preparation of useful micro-sections. A solution of citric acid as an electrolyte in the etching bath yielded good results with cupro-nickel (80:20), silver, nickel-silver, and some other metals, and it was noticed that silver and nickel-silver specimens which had been comparatively roughly treated during the polishing process often gave clearer etchings than the specimens which had been polished with great care. Certain specimens of silver showed on etching a cell structure or network which was smaller than, and in some cases independent of, the existing crystal grains. Another electrolyte made by dissolving molybdic acid in excess of ammonia solution gave somewhat similar results, and revealed a subsidiary cell formation or net-work in the beta regions of a beta plus gamma brass containing 6 per cent of aluminium. By making use of such reagents as hydrofluoric acid, chromic acid, and bromine water, both the cores (or dendrites) and the crystal grain boundaries of cast cupro-nickel were disclosed simultaneously. The paper is illustrated with 18 photomicrographs, and concludes with some notes on the etching of gold and platinum.

# NOTES.

University of Birmingham.—A Department of Brewing and of Bio-chemistry of Fermentation has been founded at the University of Birmingham. It will be in charge of the Adrian Brown Professor, Mr. Arthur R. Ling, M.Sc., and it has been established for the study of applied bio-chemistry, especially in connection with malting and brewing, and the fermentation industries generally. It deals with agriculture and cognate industries, chemistry and bacteriology as applied to food and drugs, water supply, and the treatment of sewage, &c. There is a degree course, a diploma course, certificate course for brewers and maltsters who are unable to devote the time to study required for the diploma course, and shorter courses of lectures and practical work in the principles of malting and brewing. There are also facilities for training in agricultural chemistry, the chemistry of foods and drugs and of water, and the chemistry of bacteriology and sanitation.

A New Synthetic Resin from Benzylaniline.—Continuing his researches on the synthesis of resinous compounds, starting from the secondary amines in which a compound of the benzyl group figures, Mr. W. Herzog placed 9 grms. of benzylaniline in suspension in a mixture of 10 grms. of 40 per cent formic aldehyde; 20 grms. of water, and 1 cm. of concentrated hydrochloric acid, heated during an hour under a slight reflux. The supernatant solution, which has a strong odour of benzylic aldehyde, is poured out and the resinous matter deposited on the bottom of the vessel, washed several times in hot water, and then dried at about 110° C. Thus a hard, brittle, transparent substance of an amber colour, resembling colophony, is obtained. The yield is about 8·5 per cent. The resin is soluble cold, to the extent of 25 per cent in benzol, as also in trichlorethylene, giving very stable solutions. It is very suitable for making resisting lacquers. In spirit of turpentine the resin is only soluble hot.—*Rev. Chim. Industr.*, August, 1921.

## NEW COMPANIES.

The under-mentioned particulars of New Companies recently registered are taken from the Daily Register compiled by JORDAN & SONS, LIMITED, Company Registration Agents, Chancery Lane, W.C 2.

PILE FABRIC MANUFACTURING COMPANY, LIMITED.—(176633)—Hill Top Works, Allerton, Bradford. Registered September 5th, 1921. To carry on the business of Spinners, Manufacturers, Dyers and Finishers and Merchants of Velvet Plush, Worsted, Woollen and other Textile goods. Nominal Capital: £12,000 in 12,000 Ordinary Shares of £1 each. Directors: To be appointed by Subscribers. Qualification of Directors: £1. Remuneration of Directors: To be voted by Company in General Meeting. Subscribers: A. Oddy, Ryecroft House, Drighlington, Near Bradford; G R. Allan, 186, Salt Street, Manningham, Bradford.

LENGS, LIMITED.—(176617)—Registered September 3rd, 1921. 205, High Street, Acton, W.3. To carry on the business of Chemists and Druggists Nominal Capital: £1,000 in 1,000 Shares of £1 each. Directors: A. E. Leng, 205, High Street, Acton, W 3. (Chairman); Nellie Leng, 205, High Street, Acton, W.3. Qualification of Directors 1 Share. Remuneration of Directors· To be voted by Company in General Meeting.

BEARD & Co., LIMITED.—(176658)—Registered September 7th, 1921. The Pennycomequick Pharmacy, Saltash Road, Plymouth. To acquire and carry on the business of Chemists and Druggists. Nominal Capital: £500 in 500 Shares of £1 each. Directors: Mrs. Florence S. Beard, 6, Winston Avenue, Plymouth (Chairman and Managing Director); Gwendolen C. Lewthwaite, 1, Upper Knollys Terrace, Alma Road, Plymouth; T. S. Eyre, 6, Clarendon Place, Citadel Road, Plymouth. Qualification of Directors· £10. Remuneration of Directors: To be voted by Company.

## New Patents.

THIS List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W.C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

24139—Baddiley, J.—Manufacture of 1: 4 naphthol sulphonic acid. September 10.

23724—Baker & Sons and Perkins, Ltd., J.—Manufacture of paper for filtering. September 6.

23741—Casale, L.—Process for synthetic production of ammonia. September 6.

23964—Craig, E N.—Production of oxides of tungsten and molybdenum. September 8.

23637—Vaines, R.—Process for rendering chlorides of ketone soluble by means of alkalies. September 5.

*Specification published this Week.*

144306—American Smelting and Refining Co.—Method of making sulphur dioxide.

*Abstract Published this Week.*

*Potassium Chloride and Sulphate.*—Patent No. 166657.—A process for the recovery of potassium salts from the waste liquor obtained in the rum industry has been Patented by Mr. M. Bird, of Port Mourant, Berbice, British Guiana. After crystallizing out the cane sugar and distilling of the rum, waste heat produced in the factory is employed to effect the evaporation and charring. The liquor, which is first preferably neutralized with leave, may be concentrated by passing it slowly over the heated flues leading from the furnaces to the factory chimney, and is then poured into metallic pots. These are placed inside the flues to cause their contents to char. The residual mass has a content of phosphoric acid and nitrogen and is used as such as a manure, or the potassium chloride and sulphate may be leached out with water. Alternatively, the liquor concentrated as above described may be charred or incerated by other means.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

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# THE CHEMICAL NEWS.

VOL. CXXIII., No. 3208.

## BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

EDINBURGH, 1921.

## DISCUSSION ON THE AGE OF THE EARTH.*

### I. *Opening Remarks.*

By the Right Hon. LORD RAYLEIGH, F.R.S.

IN view of the past history of this subject, it seems particularly important to keep our eyes open to all possibilities, and to welcome evidence from any quarter. Lord Kelvin in the last generation, attempted to set a limit of time to the duration of the sun's heat. And also, from consideration of the earth's internal heat, he argued back to the time when the surface was too hot for the presence of living beings.

As regards the earth's heat, it is now generally known that the premises of Lord Kelvin's calculations, carefully particularised by him, are upset by the discovery of radioactive substances in the earth. In 1906, I made a determination of the amount of radium in the superficial parts of the earth which are alone accessible. From the radium analysis we can calculate the amount of uranium and other associated substances, and the thermal output from them. The result is to show that if we suppose the same radium content to extend to a depth of some 20 miles, the whole output of heat would be accounted for, without assuming that any of it comes from primeval store as postulated by Lord Kelvin. It is surprising, in fact, that the output is not greater. We are puzzled at the present time to account for the existing state of things, and cannot use it as a firm basis from which to explore the past.

Next, as to the sun's heat. Lord Kelvin's argument was that we knew of no source at all adequate to supply the existing output of solar energy except secular contraction; and even this was not enough to account for more than 20 million years of solar heat in the past. Although we still do not know definitely of such a source, yet we are now compelled to admit that it must exist. Some of the stars (the giant red stars) are radiating energy at something like 1,000 times the rate that the sun does. They ought, according to the contraction theory, to have expended an appreciable fraction of their total energy in historical times. No one will maintain that this has occurred, and if not, there must be some source of supply other than contraction. If this is admitted, Lord Kelvin's argument from the sun's heat fails.

Modern knowledge in radioactivity, on the other hand, seems to give a firm basis for the estimation of geological time. Uranium, for example, goes through a series of changes (radium is one of the stages in its progress), changing eventually into an isotope of lead—that is, an element chemically indistinguishable from lead except a slight difference in atomic weight, and inseparable from ordinary lead by chemical means if once mixed with it. The isotope in question has probably an atomic weight of 206 exactly, as contrasted with 207·1 for ordinary lead, which is doubtless to some extent a mixture of isotopes. Thus the product has a much less atomic weight than uranium (238·5), and the difference represents approximately the weight of helium atoms, which are the debris shed at the various stages of the transformation.

Further, it is well established that a grm. of uranium as found along with its products in rocks and minerals is now changing at a rate represented by the production of $1 \cdot 88 \times 10^{-11}$ grms. of helium and $1 \cdot 22 \times 10^{-10}$ grms. of lead isotope per annum. There is every reason to believe that this is also the rate at which 1 grm. of uranium has changed in the past, since the rate is unaffected by any change of temperature or pressure which we can apply.

Minerals containing uranium are always found to contain helium and lead. The helium may safely be treated as wholly a radioactive product. It would be difficult to account for its presence, retained mechanically in the mineral, in any other way. The lead in some cases conforms itself to the expected atomic weight of 206, about one unit lower than common lead, and in such cases we may safely regard the whole of it as a product of uranium disintegration.

Thus, take the broggerite found in the pre-Cambrian rocks at Moss, Norway. The lead in this monad has an atomic weight of 206·06 as determined by Hönigschmid and Fräulein St. Horovitz. The ratio of lead to uranium is 0·113. Taking the lead as all produced by uranium at the rate above given, we get an age of 925 million years. Some minerals from other archæan rocks in Norway give a rather longer age. A determination of the amount of helium in minerals give an alternative method of estimating time. But helium, unlike lead, is liable to leak away, hence the estimate gives a minimum only. I have found in this way ages which, speaking generally, are about one-third of the values which estimates of lead have given, and are, therefore, generally confirmatory, having regard to leakage of helium. This method can be applied to material found in the younger formations. Thus the helium in an eocene iron ore indicated 30 million years at least.

H. N. Russel has recently applied the argument from accumulation of lead to the earth's crust as a whole. He takes the uranium as $7 \times 10^{-6}$ of the whole, the lead as $22 \times 10^{-6}$ of the whole. If all the lead were uranium lead, and had been generated since formation of the crust, the time required would be $11 \times 10^{9}$ years. This is certainly too great. Allowing for the production of some of the lead by uranium, Russel finds $8 \times 10^{9}$ years as the upper limit. This is about six times the age indicated by the oldest individual radioactive minerals that have been examined.

The upshot is that radioactive methods of estimation indicate a moderate multiple of 1,000 million years as the possible and probable duration of the earth's crust as suitable for the habi-

*British Association, Edinburgh Meeting (Sections A, C, D, K.).

tation of living beings, and that no other considerations from the side of physics or astronomy afford any definite presumption against this estimate. The argument from geology and biology I must leave to our colleagues from other sections. May I venture to say that I for one consider the topics with which they will deal as not less interesting and important than those which it has been my privilege to lay before you?

2. *Remarks by* Prof. J W. Gregory, F.R.S.

The claim that geological time must be restricted within a score or a few score million years was regarded by most geologists with incredulity, since a score million years was of little more use to geology than the seven days of the Pentateuch. Now that physical evidence allows the age of the earth to be counted by the thousand million years, the problem is of less concern to the geologist, except from the hope that the uranium-lead ratio may fix geological dates in years, and from the interest of reconciling the conflicting results of the different methods.

The geological estimates to which most weight has been attached are based on the saltness of the sea. The salinity argument has been widely accepted as sound in principle; the estimates varied from 70 to 150 million years, and some intermediate length was regarded as inevitable. Allowances were made for various factors; but they added only a few per cent to the total, and did not multiply it by 10 or more.

The validity of the salinity argument may be tested by two checks—the supply of chlorine, and the denudation required to account for the amount of sodium; and as shown by Dr. A. Holmes, each of these indicates a much longer period than the sodium.

The supply of chlorine in igneous rocks is quite inadequate to convert their sodium into chloride. Most of the sodium chloride in river water is probably marine in origin, and only the sodium in the bicarbonate and sulphate is a fresh addition to the sea. On this ground the salinity estimate should be approximately doubled. Again, to obtain all the sodium in the sea from igneous rocks would involve the denudation of improbable volumes of them, and, at the rate usually accepted, the age of the earth should be multiplied three- of four-fold.

The fundamental objections to the salinity argument are against (1) its assumption that the sea was originally fresh, which palæontological evidence renders improbable. The oldest fauna, the Cambrian, has the characteristics of a marine fauna, and the contrast between the fresh-water and marine faunas was as sharp in Palæozoic times as it is to-day. (2) Its omission to allow for the large supplies of sodium chloride raised from beneath the earth's surface by magmatic waters. (3) Its assumption of uniform denudation. The earth has probably undergone deformations that led to alternate periods of quick and slow crustal movement; during the times of repose the surface would have been planed down, rivers would have become sluggish and denudation slow. As the earth is now under the influence of a time of quick movement, denudation is faster than the average. A multiplication of the earth's age five-fold for this difference would not be excessive.

During quick crustal movement volcanic action would be more powerful, and the discharge of hydrochloric acid and sodium in hot springs would be increased; and as denudation is now acting on land in which sodium chloride has been produced in unusual quantities by volcanic action the estimated age of the earth must be again extended. The rythmic acceleration of geological processes lengthens the estimates based on sedimentation, but would affect the biological argument inversely, since at periods of rapid physical change biological change would have been quickened, and thus the occasional abrupt introduction of a new fauna does not necessitate so long an interval as has been thought.

The best-known geological estimates of the age of the earth require to be multiplied ten- or twenty-fold in order to agree with the physical estimates, but this increase is consistent with the geological evidence.

3. *Remarks by* Prof. A. S. Eddington, F.R.S.

A study of the Cepheid variable stars affords strong evidence that the stars have other sources of energy besides that furnished by gravitational contraction. The rate of radiation by δ Cephei is such that it would be necessary for the density to increase 1 per cent in 40 years in order to provide the required energy. The light-change of δ Cephei is believed to be due to a periodity intrinsic in the star (*e.g.* pulsation); it is clear that such an intrinsic period cannot remain unaltered whilst the density changes so rapidly. But the observed change of period of δ Cephei is only $0^{s}{\cdot}08$ per annum, or 1 per cent in 58,000 years. The condition of δ Cephei is thus changing at a rate very much slower than that required by the contraction theory. The figures suggest that Lord Kelvin's time-scale should be lengthened 500-fold —at least during this stage of the evolution.

## NON-AROMATIC DIAZONIUM SALTS.*

Recent investigations have shown that several series of non-aromatic primary amines possess in varying degrees the property of diazotisability. In certain cases, the existence of a diazo-derivative is inferred from the property of coupling to form azo-derivatives or from the fact that the diazo-group can be replaced by other radicals such as chlorine, but in other instances diazonium salts have actually been isolated. These non-aromatic diazonium salts vary considerably in stability from the exceptionally stable diazonium salts of the pyrazole series to the explosive diazo-derivatives of the thiazole group. Orientation plays an important part in the stability of these compounds, as is shown below in the case of the pyrazole and pyridine derivatives.

The requisite properties for diazotisability appear to be the presence of the group $H_2N—C\Big\langle$ and the possession of a certain degree of unsaturation in the cyclic system in which this carbon atom is included. But it must not be assumed that any base having the foregoing group and belonging to an unsaturated cyclic system is necessarily diazotisable. The absence of diazotisability is noteworthy in the thiophen,

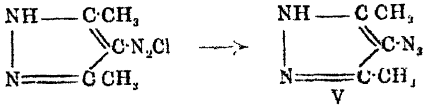
*Report of Committee, consisting of Dr. F. D. Chattaway (Chairman), Prof G. T. Morgan (Secretary), Mr. P. G. W. Bayly and Dr N V. Sidgwick. Drawn up by Prof. G. T. Morgan and Mr Henry Burgess. Presented at British Association, Edinburgh Meeting (Section B).

furane, and pyrrole series in spite of the close relationship between the first of these series and the aromatic compounds.

*Pyrazole Series.*—In this group the effect of orientation on the stability of the diazonium salts is well marked. 4-amino-3 : 5-dimethylpyrazole when diazotised in the usual manner furnishes 3 : 5-dimethyl pyrazole-4-diazonium chloride stable in hot aqueous solutions and up to 150° C. in the dry state This salt, which retains its diazo nitrogen and coupling power for an indefinite time, gives rise to sparingly soluble diazonium platinichloride and aurichloride (Morgan and Reilly, *T.*, 1914, cv., 435). Other 4-aminopyrazole derivatives yield similarly stable diazo-derivatives (Knorr, *B.*, 1895, xxviii., 717; Michaelis and Schafer, *A.*, 1915, cdvii., 229; Michaelis and Bressel, *A.*, 1915, cdvii., 274).

When the diazonium group is in position 5 the product is distinctly less stable, for 1-phenyl-3-methyl-4-ethylpyrazole-5-diazonium chloride decomposes at room temperature in a few hours, and quickly on warming (Mohr, *J. Pr. Chem.*, 1914, (2) xc , 509). 1-phenyl-3-methyl-5-amino-pyrazole I containing a labile hydrogen atom in position 4 gives only 12 per cent of diazonium compound (Mohr, *loc. cit.*) (see Fig. 1).

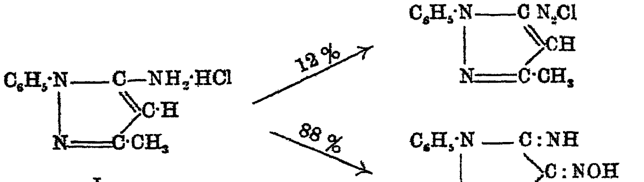
In this series replacement of the diazonium complex by iodine (Knorr, *loc. cit.*) and by the triazo group has been effected. It is noteworthy that 4-triazo-3 : 5-dimethylpyrazole V, a well-defined crystallisable compound, has the remarkable property of giving distinctive colour reactions with all phenolic substances not containing nitro-groups (Fig. 4).



V

FIG. 4.

*Pyrazolone Series.*—Very stable salts are obtained on diazotising the hydrochlorides of the amino-pyrazolones; the products are crystallisable from hot aqueous solutions, and are stable in a dry state for an indefinite time (Knorr and Geuther, *A.*, 1896, ccxciii., 55; Knorr and Stolz, *A.*, 1896, ccxciii., 58; Michaelis, *A.*, 1906, cccl., 288). The acid diazonium salts, VI., from amino antipyrine (Morgan and Reilly, *T.*, 1913, ciii., 808, 1494) are exceptionally stable and recrystallisable and in these respects are unlike the decomposable acid diazonium salts of the aromatic



I

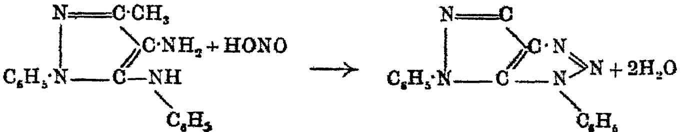
FIG. 1.

series (Hirsch, *B.*, 1897, xxx., 1148; Hantzsch, *ibid.*, 1153). Double salts with auric chloride and platinic chloride have been prepared and are stable up to 120° C. in the dry state (Morgan and Reilly, *loc. cit.*) (Fig. 5).

Diazoamino derivatives are formed with fatty amines such as dimethylamine, and are stable up to 120° C., when they begin to decompose into the amine and a complex pyrazolone derivative, the constitution of which has not been settled (Stolz, *B.*, 1908, xli., 3849). In this series, as in the

Substitution of the labile hydrogen by an alkyl group prevents the second reaction, and diazotisation takes place quantitatively.

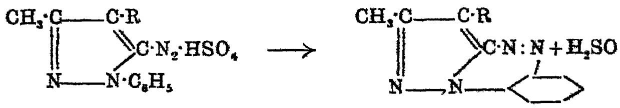
In the case of 1-phenyl-3-methyl-4-amino-5-anilinopyrazole an azimino compound II is formed unless diazotisation is carried out in strong acid (Michaelis and Schafer, *loc. cit.*) (Fig. 2).



II

FIG. 2.

On adding a solution of any diazonium salt of the general formula III to boiling dilute sulphuric acid the diazonium nitrogen is retained and a triazine IV is produced (Fig. 3).



III IV

R = an alkyl group.

FIG. 3.

pyrazoles, the diazonium complex has been replaced by iodine (Michaelis, *loc. cit.*), and by the triazo group (Forster and Muller, *T.*, 1909, xcv., 2072) VII, but reduction with stannous chloride does not lead to a readily isolated hydrazine, probably owing to condensation taking place with the carbonyl group in the ring (Morgan and Reilly, *loc. cit.*).

to dryness in vacuo over potassium hydroxide, a colourless *iso*diazo hydroxide is obtained, which is quite stable at 100° C., and couples only after being acidified. The diazonium complex is replaced by hydrogen on reduction with alcohol, and with stannous chloride the hydrazine is obtained (Thiele and Manchot, *loc. cit.*).

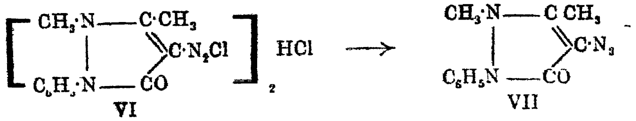



FIG. 5

*Iso-oxazole Series.*— 4-amino-3·5-dimethyl*iso*oxazole has recently been prepared and diazotised. The diazonium chloride VIII is very soluble and is much less stable than the corresponding pyrazole compound. The diazonium aurichloride is sparingly soluble and stable on keeping in the dry state at the ordinary temperature (Morgan and Burgess, *T.*, 1921, cxix., 697) (Fig. 6).

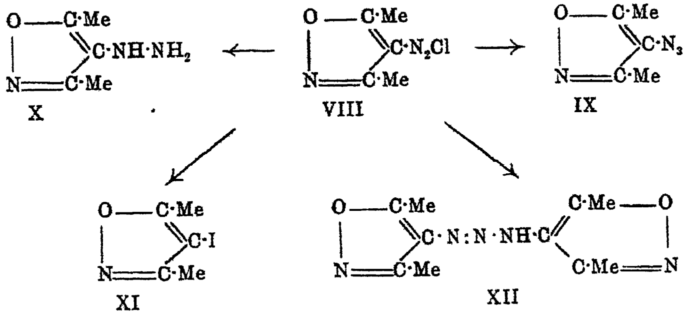



FIG. 6.

The diazonium complex is readily replaced by the triazo group IX and by iodine XI. The diazonium chloride reacts, with the base forming a well-defined colourless diazoamine XII, and is reduced by stannous chloride to the hydrochloride of the hydrazine X.

*Glyoxaline Series.*—The bases of this group have not been studied exhaustively as regards diazotisability, but 2-aminoglyoxaline when treated successively with nitrous acid and alkaline $\beta$ naphthol gave a brownish-red, soluble azo-derivative, which does not appear to have been isolated (Pyman and Fargher, *T.*, 1919, cxv., 247).

*Triazole Series.*—When 5-aminotriazoles are diazotised in hydrochloric acid solution, the resulting salt decomposes fairly quickly at 0° C. into nitrogen and the corresponding chlorotriazole (Thiele and Manchot, *A.*, 1898, ccciii., 33) If, however, oxy-acids are used instead of hydrochloric acid, more stable diazonium salts are obtained, although these are too unstable to be isolated (Morgan and Reilly, *T.*, 1916, cix., 155) The sparingly soluble diazonium aurichloride has been isolated and is stable in the dry state. When a solution of the diazonium nitrate is evaporated to dryness in vacuo over potassium hydroxide, a colourless *iso*diazo hydroxide is obtained, which is quite stable at 100° C., and couples only after being acidified.

*Thiazole Series*—2-Aminothiazole reacts in the same way as aminotriazole with nitrous acid. In hydrochloric acid solution an unstable diazonium chloride is produced. This decomposes rapidly at 0° C. into nitrogen and chlorothiazole. Oxy-acids give more stable salts, especially sulphuric acid. The perchlorate is explosive even at 0° C. The yellow diazonium aurichloride is sparingly soluble, and is stable in the dry state, but becomes brown on washing with water. In feebly acid solution aqueous sodium nitrite gives an unstable orange-red powder, probably an *isodiazo* compound (Morgan and Morrow, *T.*, 1915, cvii., 1291). Reduction of the diazonium sulphate with alcohol causes the replacement of the diazonium complex by hydrogen (Hantzsch and Popp, *A.*, 1889, ccl., 274).

*Pyridine and Quinoline Series*—Nitrous acid acts on the amines derived from these bodies in the same way. The $\alpha$ and $\gamma$ amines when treated in hydrochloric acid solution yield forthwith the corresponding chloro derivatives. This reaction suggests a rapid decomposition of a probable intermediate diazonium chloride (Marckwald, *B.*, 1898, xxxi., 2496; *B.* 1894, xxvii., 1325; H. Meyer, *Monatsch.*, 1894, xv., 173; Claus and Howitz, *J. Pr. Chem.*, 1894, (2) l., 23). Oxy-acids have not been used and these would probably give better results. The $\beta$-amines form diazonium chlorides, which do not appear to have been isolated but have been coupled with phenols (Mohr, *B.*, 1898, xxxi., 2495; Watson and Mills, *T.*, 1910, xcvii., 743). The corresponding $\beta\beta$-diazoaminopyridine is a yellow, crystalline, stable compound (Mohr, *loc. cit.*).

## THE SPECTRA OF HYDROGEN FROM LONG VACUUM TUBES.*

By PROF. R. W. WOOD, For.Mem.R.S.

THE spectrum of hydrogen obtained in the laboratory exhibits a Balmer series of lines, of which only twelve members are found under ordinary conditions. Thirty of the lines have been recorded in the solar spectrum. The impossibility of obtaining the higher members of the series in the laboratory results, in part at least, from the presence of a continuous spectrum and the so-called secondary sepctrum.

By employing vacuum tubes of unusual length it has been found that the secondary spectrum appears only at the ends, the central portion radiating a very pure Balmer spectrum. By this means it has been possible to record the series down to the twentieth line. Very remarkable phenomena have been observed with tubes of this type. Starting with a very feeble current, the secondary spectrum only is in the tube, the Balmer lines being absent. As the current is increased the Balmer lines appear and increase in intensity, while the secondary spectrum fades away, passing through a minimum value of about one-fiftieth of the intensity shown at the ends of the tube, after which it slowly increases in intensity.

If a heavy current is employed, there is an explosive flash of the secondary spectrum at the moment of closing the switch, the Balmer lines being feeble. In about one-sixtieth of a second, the secondary spectrum has nearly disappeared (reduced to one-fiftieth of its initial value) and the Balmer lines have risen to full intensity. These phenomena occur only when a trace of oxygen or water vapour is present. With pure hydrogen, continued operation of the tube eventually causes the complete disappearance of the Balmer series, the secondary spectrum remaining, and the colour changing from fiery purple to white. A new spectrum has been found which is much more complicated in structure than the secondary spectrum. This appears when the tube is in the condition best suited to the exhibition of the Balmer series.

## THE RECEPTION OF WIRELESS WAVES ON A SHIELDED FRAME AERIAL.*

By ALAN A. CAMPBELL SWINTON, F.R.S.

THE paper describes experiments in receiving the spark emission from the Eiffel Tower on a small frame aerial placed inside a tube of wire network with open ends. It was hoped to obtain improved directional properties, but, though the presence of the tube weakened the signals, it was found that altering its direction did not affect them, nor were the signals further weakened by closing the open ends of the tube by wire grids.

The tube was next replaced by a sheet copper box with one open end. In this was placed, not only the frame, but also the amplifier and all the other apparatus, the telephone being listened to through a rubber pipe. Signals were heard of equal strength with the open end of the box pointing towards, or directly away, from Paris; but ceased when the box was turned so that the open end faced at right angles to Paris, the frame still pointing to Paris; or when the open end was completely closed with copper or tinfoil cover. In the latter case the signals were still audible unless the cover actually touched the box on all sides. For other positions of the box with the end open, signals could only be heard when the relative positions of the box and frame were such that a prolongation of the plane of the frame towards or away from Paris, no matter which, came out of the open end clear of the copper sides of the box.

*Read before British Association, Edinburgh Meeting (Section A).

## THE NORWEGIAN INDUSTRIES FAIR.

THIS Fair, held in Christiania, September 4—11, appears to have been highly successful. From an account sent to us by Dr. Sebilien, much business appears to have been done; buyers came from practically every country in Europe and overseas; the number of exhibitors was double that of last year, and the area of the Exhibition was much greater.

The capital purpose of the Fair was to promote the sale of Norwegian products in home and foreign markets

The Chemical Industry, particularly the manufacture of sulphuric acid and fertilisers, is active, and is largely helped by the abundance of water-power. The Norwegian waterfalls are said to be capable of producing ten million horse-power.

Electricity was well represented in the Fair; there was a good show of dynamos and electric heating appartus.

Cellulose, paper pulp, rubber, and ebonite wares and coal-tal products were shown.

At a meeting of Norwegian merchants and financial representatives, the situation of the export trade of the country was discussed. Although Norway has been gifted with a lot of raw stuffs (about every chemical element except tin and mercury is found in Norway), and with more energy in its waterfalls than any other country in Europe, it was statistically shown that few nations have to seek their conditions for living outside its own frontiers more than the Norwegian. All the Norwegian industry of machinery and a very great part of its chemical industry is based on shipping and export. The lucky geographical situation of the country in connection with its many lucky conditions for export will in the long run come forward and bring up the country from the difficulties that just now are predominating.

It was suggested that the Norwegian Industrial Fair ought to be a fixed annual institution, and in connection with the same, should grow up an opening term for sale of the more essential part of the Norwegian export trade—paper and paper-pulp, trade in fish oil, &c.

SIR JOHN CASS TECHNICAL INSTITUTE.—A new development in the activities of this Institute is the introduction of a course of lectures in Petroleum Technology. The course will be opened by a special lecture at the Institution, Jewry Street, Aldgate, E.C., on Monday, October 10, at 7 p.m., by E. H. Cunningham, Esq., B.A., F.R.S.E., M.Inst.P.T., F.G.S., on the "Geology of Petroleum." The Chair will be taken by Sir Frederick Black, K.C.B.

# GERMANIUM.*

## I.—Occurrence; Extraction from Germanium-bearing Zinc Oxide; Non-Occurrence in Samarskite.

By L M DENNIS and JACOB PAPISH.

### *Historical.*

Mendeleeff, in 1871, predicted the existence of an element to which he gave the name ekasilicon. In 1885 there was discovered at the Himmelsfürst mine near Freiberg in Saxony a new mineral which Weisbach named argyrodite (*Neues Jahrb. f. Miner.*, 1886, ii., 67). Richter made a superficial examination of this mineral, and found that its chief constituents were silver and sulphur. Clemens Winkler then made careful analysis of the compound, and found that contained from 73 to 75 per cent of silver, 17 to 18 per cent of sulphur, and smaller amounts of mercury, iron, and arsenic. The sum of these constituents, however, amounted to only 93 to 94 per cent of the weight of the sample taken, and careful search for the cause of this discrepancy led Winkler to the discovery of a new element, to which he gave the name germanium (*Ber.*, 1886, xix., 210). He at first thought that this new element was an analogue of antimony, and that it would find place in the periodic system between antimony and bismuth, but von Richter, Mendeléeff, and Lothar Meyer, in separate letters to Winkler early in 1886, pointed out that the new element was very probably identical with the ekasilicon whose properties had been predicted by Mendeléeff fifteen years earlier, and this view was borne out by Winkler's later careful and brilliant experimental study of the element and its compounds (*J. prak. Chem.*, 1886, (New Series xxxiv.), cxlii., 177; 1887, (New Series xxxvi.), cxliv., 177).

Under Winkler's direction, a large amount of ore-containing argyrodite was subjected to chemical treatment for the extraction of germanium, but it was found that the material contained on an average not over 0·03 per cent of the element. The amount of germanium that he recovered was about 150 grms.

### *Occurrence.*

(*A*) *In Sulphide Materials.—In Argyrodite.*—The mineral argyrodite is of rare occurrence, and no further appreciable amount of it has been furnished by the Freiberg district since Winkler's investigation in 1885. It is a sulphide of silver and germanium corresponding in composition to the formula $4Ag_2S.GeS_2$, with a germanium content of about 7 per cent. In 1893 Penfield (*Amer. Jour. Sci.*, 1893, (3), xlvii., 107) announced the discovery of argyrodite in Bolivia, stating at the same time that very little was known concerning the exact locality and mode of occurrence of this mineral.

It is of interest to note that two mineral specimens which had been found in Freiberg in 1817 and in 1821, respectively, were identified, one by Kolbeck (*Zentrb. f. Min. u. Geol.*, 1908, 331), and the other by Frenzel (*Jahrb. f. Berg- u. Huttenwesen*, 1900, 61; *Chem. Zentrb.*, 1901, i., 590) as being varieties of argyrodite.

*In Canfieldite.*—This mineral, which was first described by Penfield in 1894 (*Amer. Jour. Sci.*, 1894, iii., xlvii., 451), is in reality a stanniferous argyrodite. It was discovered in La Paz, Bolivia, and upon analysis was found to correspond to the formula $4Ag_2S.(Sn.Ge)S_2$, germanium replacing tin isomorphously. The germanium content of this particular mineral was given by Penfield as 1·8 per cent, while the content of tin was nearly 7 per cent.

A stanniferous argyrodite containing almost 5 per cent of germanium was described by Prior and Spencer in 1898 (*Miner. Mag.*, 1898, xii., 5). The sample upon which they worked came from Aullagas, Bolivia. These investigators also examined a sample of the so-called brongniardite from the same locality, and found that it was nothing but a variety of stanniferous argyrodite.

*In Frankeite.*—Stelzner (*Neues. Jahrb. f. Min.*, 1893, xi., 114) proposed the name frankeite for a Bolivian mineral, the composition of which, according to Winkler (*ibid.*, p. 119), corresponds to the formula $5PbS.2SnS_2.Sb_2S_3$ He found that it contained about 0·1 per cent of germanium. Khrushchov (*Zhurnal Russkago Fiziko-Khimicheskago Ob-va-* 1892, xxiv., Sec. 1, 30) reported that he also had found traces of germanium in frankeite.

*In Blendes.*—Urbain (*Compt. Rend.*, 1909, cxlix., 602) made a spectrographic investigation of 64 samples of blendes and found that 38 of them showed the presence of germanium. Five of these contained the element in amounts sufficient to disclose all of its spectrum lines. These five richest samples came from Webb City, Missouri, Stolberg near Aachen, European Turkey (in 1909), Raibl in Austria (Urbain gives the source of this sample as "Raibl, Corinthie"; it should read "Carinthie, eng. Carinthia"), in Austria, and Mexico. In conjunction with Blondell and Obiedoff, Urbain (*Compt. Rend.*, 1910, cl., 1758) extracted germanium from Mexican blendes and obtained 5 grms. of germanium from about 550 kilogrms. of the mineral.

Hillebrand and Scherrer (*J. Ind. and Eng. Chem.*, 1916, viii., 225) subjected various zinc ores to spectroscopic examination and reported the presence of germanium in sulphides from Missouri and Idaho.

Buchan (*J. Ind. and Eng. Chem.*, 1916, viii., 585; 1917, ix., 661) found germanium in zinc oxide that had been prepared from spelter residues. It was his belief that this material had been obtained either from a Wisconsin or a Missouri ore or from a mixture of both, and that the germanium in the final product had been greatly concentrated during the metallurgical treatment to which the ore had been subjected. The amount of germanium calculated as germanium dioxide in the original ore was estimated by him to be about 0·01 per cent.

(*B*) *In Minerals Containing Titanium, Zirconium, and Columbium.*—In his prediction of the existence of ekasilicon, Mendeléeff (*Ann.*, Eigth Suppl., 1872, p. 200) expressed the opinion that this element should be looked for in complex minerals containing titanium, zirconium, and columbium. The later discovery of ger-

*Contribution from the Department of Chemistry of Cornell University. This article is based upon a part of the thesis presented to the Faculty of the Graduate School of Cornell University by Jacob Papish in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

manium and the striking agreement of its properties with those predicted for ekasilicon stimulated the search for this element in minerals of the above character.

*In Fergusonite.*—Krüss and Nilson (*Ber.*, 1887, xx., 1696) examined the fluoride residues from fergusonite, but failed to find germanium in them. Khrushchov (*loc. cit.*), on the other hand, reported that he found traces of germanium in this mineral.

*In Euxenite.*—In 1888, Krüss (*Ber.*, 1888, xxi., 131) announced the discovery of germanium in euxenite. He surmised that the germanium in this mineral replaced a part of tetravalent titanium and for this reason he took up a search for germanium in other titaniferous minerals, such as rutile, yttrotitanite, and wohlerite. The results of this investigation were never published, and it is therefore fair to assume that Kruss did not find germanium in these minerals.

Lincio (*Zentrb. f. Min.*, 1904, 142) re-examined euxenite and failed to find even a trace of germanium in the mineral. He also analysed two samples that had been left by Krüss, and that had been marked "germanium oxide" and "germanium sulphide" from euxenite residues, and found the first to consist of tantalic and columbic acids, and the second of tantalic and columbic acids and sulphur. No trace of germanium was found in either sample. This would seem to establish the fact that euxenite is not to be regarded as a germanium-bearing mineral.

*In Samarskite.*—Khrushchov (*loc. cit.*) stated that he had found in American samarskite as much as 1·5 per cent germanium. His statement was given publicity in mineralogical and chemical periodicals and from these it found its way into chemical handbooks and textbooks. The correctness of this statement was later challenged by Lincio (*loc. cit.*), and results obtained in this laboratory confirm Lincio's view (see ante).

(*C*) *In the Sun.*—In a provisional table of thirty-six elements present in the sun, Rowland ("John Hopkins Univ. Circular," No. 85; *Amer. Jour. Sci.*, 1891, xli., 243) placed germanium thirtieth in respect to the intensity of spectrum lines, and thirty-third in respect to he number of lines.

(*D*) *In Mineral Waters.*—Bardet (*Compt. Rend.*, 1914, clviii., 1278) examined various mineral waters spectroscopically, and found that germanium was present in many of them. He succeeded in extracting 60 mgrms. of germanium dioxide from about 100 kilogrms. of residues, chiefly calcium carbonate, obtained in the manufacture of Vichy salts from the natural waters. This amount of germanium dioxide represented 250,000 litres of original Vichy water, and corresponded to 0·00024 mgrms. of germanium dioxide per litre of water, a quantity too small to render these waters practicable sources of supply of germanium.

(*E*) *In Zinc Carbonate Ores.*—Hillebrand and Scherrer (*loc. cit.*) observed that some zinc carbonate ores from Colorado, Nevada, and Utah contain spectroscopic traces of germanium.

(*F*) *In Marine Plants.*—Cornec (*Compt. Rend.*, 1919, clxviii., 513), while making a spectrographic study of the ashes of marine plants, detected slight traces of germanium in the ashes of *Laminaria*.

*Experimental.*

(*A*) *Material.*—Argyrodite and canfieldite, which at present are the only materials known to contain germanium as a definite constituent, are too rare to be regarded as sources of supply of the element. The extraction of germanium from spring waters, although strongly recommended by Bardet, is at present quite impracticable, because 1 kilogrm. of the residue contains only 0·6 mgrm. of germanium oxide. The extraction of germanium directly from blendes, as has been carried out by Urbain, is a very expensive and tedious operation. The most promising source of the element at the present time is the concentrate from certain residues obtained in the smelting of American zinc ores. Buchanan (*loc. cit.*) reported that one such residue contained as much as 0·25 per cent of germanium dioxide. A large supply of this most valuable material was presented to the Department of Chemistry of Cornell University by the New Jersey Zinc Company, and the present investigation, as well as others that will follow from this laboratory, would not have been possible except for the generous co-operation of this Company. Concerning the origin of this material, Mr. W. M. Kelsey (letter to L. M. Dennis, Sept. 3, 1919), Superintendent of the Palmerton plant of the New Jersey Zinc Company, states that it was obtained "by a fire concentration of certain residues produced in the ordinary process of smelting for zinc. The original ore was a mixture of high-grade sulphides from the Wisconsin and Missouri fields, roughly in the ratio of two parts of Wisconsin ore to one part of Missouri ore."

(*B*) *Extraction of Germanium.*—None of the various methods that were employed by Winkler for the extraction of germanium from argyrodite are adapted to the separation of the element from the germanium-bearing zinc oxide, because the association of elements in this latter material is quite different from that in argyrodite. Zinc oxide is, of course, present in preponderating amount, and the concentrate further contains considerable quantities of lead, arsenic, and cadmium, and also traces of other elements, among them being indium, tin, and antimony.

Preliminary trials were made of a variety of possible methods of separation, but as none of these was found to be satisfactory, descriptions of them will not here be given. The procedure that was finally adopted is based upon the volatility of germanium tetrachloride, and is an elaboration of the method described by Buchanan (*J. Ind. and Eng. Chem.*, 1916, viii., 585). The essential feature of this process consists in treating the crude zinc oxide with hydrochloric acid and then distilling off germanium tetrachloride in a current of chlorine. The chlorine maintains the arsenic in pentavalent form, and thus prevents the distillation of arsenic trichloride with the germanium tetrachloride.

In the first trials of this method, portions of the crude zinc oxide of from 250 to 1000 grms. each were treated with hydrochloric acid, chlorine gas was passed through the apparatus, and the mixture was heated to effect the distillation of the germanium tetrachloride. This gave a product substantially free from arsenic, but the necessity for long passage of large amounts of chlorine through the apparatus rendered the procedure un-

suited to the extraction of germanium on a large scale from several hundred pounds of the crude material. Browning and Scott (*Amer. Jour. Sci.*, 1917, (4) xliv., 313; 1918, xlvi., 663) substituted potassium permanganate, manganese dioxide, potassium chlorate, or potassium dichromate for chlorine. They used the method for the detection of germanium in very small samples that contained less than a grm. of $As_2O_3$ or $As_2O_5$, and not more than 5 mgrms. of germanium. But even so they found that when from 0·3 to 0·5 grm. of $As_2O_3$ was used, some arsenic appeared in the distillate. It is apparently essential that if the formation of arsenic trichloride and its consequent appearance in the distillate are to be avoided, the concentration of chlorine must be high throughout the whole distillation. Fresenius (*Zeit. f. anl. Chem.*, 1862, i, 447) states that when a mixture of sodium arsenate and concentrated hydrochloric acid is distilled, small amounts of arsenic are volatilised. Mayrhofer (*Liebig's Ann.*, 1872, clviii., 326), in attempting to remove arsenical impurities from hydrochloric acid noticed that even when the acid was first treated with chlorine or when some pyrolusite was added to the acid and it was then distilled, small amounts of arsenic were always found in the distillate. Hehner (*Analyst*, 1902, xxvii., 268) distilled arsenic acid with strong hydrochloric acid, and obtained comparatively large quantities of arsenic in the several fractions of the distillate. He states that "a similar result was obtained when potassium permanganate had been added before the beginning of the distillation, or, in other words, when the distillation was begun in the presence of chlorine."

In an investigation of the reaction between hydrogen sulphide and arsenic pentoxide in the presence of hydrochloric acid, Usher and Travers (*Jour. Chem. Soc.*, 1905, lxxxvii., 1370) studied the reaction between arsenic pentoxide and hydrogen chloride in sealed tubes. They concluded that the reaction is that expressed by the equation

$As_2O_5+10HCl \rightleftharpoons 2AsCl_3+2Cl_2+5H_2O$, the equilibrium shifting rapidly to the right with increasing concentration of hydrogen chloride.

These observations upon the reduction of arsenic pentoxide by concentrated hydrochloric acid and volatilisation of arsenic trichloride when such a mixture is distilled, have been sustained by the experimental evidence accumulated in this laboratory during the progress of the investigation here described. When potassium permanganate was added to the crude zinc oxide, and this was then distilled with an excess of concentrated hydrochloric acid, arsenic trichloride passed into the distillate. To maintain the concentration of chlorine, the procedure was modified by slowly running into the flask a solution of the potassium permanganate during the distillation with hydrochloric acid. It was found that the dilution of the acid soon rose to such an amount that the germanium tetrachloride instead of distilling off was hydrolysed in the flask. To ascertain whether a mixture of sodium arsenate and sodium germanate, when distilled with an excess of concentrated hydrochloric acid, would yield arsenic trichloride in the distillate, a mixture of the oxides of arsenic and germanium was fused with a slight excess of sodium peroxide, the fused mass was dissolved in water, and the solution was heated to boiling. It was then cooled, an excess of hydrochloric acid was added, and the liquid was distilled. The distillation gave a yellow precipitate, with hydrogen sulphide which indicated the presence of arsenic. In another experiment lead dioxide was used in place of sodium peroxide. Arsenic here also passed into the distillate. These experiments, as well as the observations of previous investigators, indicate that if the volatilisation of arsenic acid is reduced to arsenic trichloride during distillation with hydrochloric acid unless high concentration of chlorine throughout the distillation is maintained.

In checking the accuracy of this separation of arsenic from germanium by distillation, it was further necessary to ascertain whether arsenic trioxide when dissolved in sodium hydroxide, saturated with chlorine, and then acidified with hydrochloric acid, would yield any arsenic trichloride when distilled in a current of chlorine.

This was tested experimentally by dissolving 5 grms. of arsenic trioxide in 20 cc. of a 30 per cent solution of potassium hydroxide, saturating this solution with chlorine, and then, without interrupting the current of chlorine, adding 190 cc. of pure concentrated hydrochloric acid, and distilling. A Reitmair-Stutzer bulb was used to prevent, so far as possible, the mechanical passage of some of the liquid into the distillate. Two fractions of 40 cc. each were obtained. Each of these was saturated with hydrogen sulphide. After twelve hours there separated a few small yellow particles that resembled sulphur. These were removed with the aid of a glass rod, and were treated with nitric acid, the acid being warmed over a small flame. The particles melted and coalesced, forming a globule about 1 mm. in diameter. On cooling, this solidified to a hard yellow particle, which was in all probability sulphur, but it was tested for arsenic by adding ferrous sulphate to reduce the nitric acid, then adding dilute sulphuric acid, warming the mixture to remove oxides of nitrogen, and finally subjecting the material to the "modified Gutzeit test" (Dennis and Whittelsey, "Qualitative Analysis," revised edn., p. 31). The reaction was allowed to proceed for ten minutes, but no discolouration of the crystal of silver nitrate was discernible.

To ascertain whether there might still be a trace of unprecipitated arsenic in the two fractions of the distillate, which was somewhat milky because of liberated sulphur, they were united and placed in a small distilling flask that was provided with a separatory funnel. Several portions of nitric acid were successively added through the funnel and the liquid was boiled until almost all chlorine was removed. More nitric acid was then added, and the solution was evaporated almost to dryness. This was then subjected to the Gutzeit test in the manner above described. A very slight yellow colouration of the crystal of silver nitrate appeared at the end of fifteen minutes. This may indicate that a mere trace of arsenic passes over as arsenic trichloride under the above conditions, or that a minute amount of the solution was carried over mechanically.

In the above experiments, blank tests showed the absence of arsenic in the hydrogen sulphide, and a trial of the Gutzeit method, in which a

minute quantity of arsenious sulphide was added, yielded at once a strong, positive result, the crystal of silver nitrate beginning to darken immediately and becoming black at the edges after only a few moments.

Müller (*Journ. Am. Chem. Soc.*, 1921, xliii., 1085), in a recent article upon the atomic weight of germanium, states that "the chlorine-hydrochloric-acid distillation process, though adequate for the removal of silica and tin, can hardly be accepted as a means of eliminating the last traces of arsenic from germanium compounds Four redistillations of the chloride from hydrochloric acid solution in a stream of chlorine failed to remove the last of the arsenic." Careful perusal of his article fails to reveal experimental support for this statement. In fact, in his description of the purification of germanium, he remarks that the precipitation of redistilled germanium tetrachloride by hydrogen sulphide yielded a "snow-white germanium sulphide." The point is of importance, and the possible presence of arsenic in the distilled germanium tetrachloride will be carefully followed during a further work in this laboratory. Inasmuch as only a very faint trace of arsenic was found in the distillate from $As_2O_3$ in hydrochloric acid in a current of chlorine, it is probable that a second distillation of germanium chloride in a rapid current of chlorine will yield a product free from arsenic.

To avoid the necessity for the use of the very large amounts of chlorine that would be called for if the germaniferous zinc oxide were directly distilled with hydrochloric acid in a current of chlorine for the separation of germanium, it was decided to distil off germanium tetrachloride and arsenic trichloride together from the crude zinc oxide and thus to effect, as a first step, the separation of the germanium from the large amount of the zinc oxide that is present in the original material.

*Apparatus.*

The unit still consists of a round-bottom 5-litre Pyrex flask that is supported on an asbestos "collar" 10 cm. high, the collar resting on an iron plate and this on a strong tripod. (This device for heating glass or porcelain vessels that contain a mixture of liquid and solid materials has been in use in the Cornell Laboratory for several years. A "collar" is made from asbestos board ⅛in. to ¼in. thick, a strip of the board of the desired width being first thoroughly wet with water, then bent into a circle and fastened at the overlapping ends with iron or copper wire, and finally dried. The "collars" may, of course, be made of any desired diameter. The collar is placed upon an iron plate about ⅛in. thick, and this plate rests in turn upon an iron tripod. If the collar is dipped in a dilute solution of sodium silicate, it becomes stiff when dry, and although somewhat brittle, its life is prolonged by the treatment A glass flask or porcelain evaporator placed on one of these collars does not come into direct contact with the gas flames under the iron plate, and local heating that would result from the direct application of the flame to the container, which often causes the fracture of the vessel, is thus avoided. The collar is especially useful in the long digestion of a powdered mineral with acids.) A two-hole rubber stopper in the neck of the flask carries a bent glass tube for connection with a Liebig condenser, and through the other opening of the stopper is inserted a short glass tube through which the desired amount of concentrated hydrochloric acid may be blown into the flask by air pressure from a large, graduated bottle. After the acid has been driven into the flask in the actual operation, the glass tube is replaced by a solid glass plug. A bent glass tube is attached to the further end of the condenser by means of a short piece of rubber tubing. This glass tube is about 10 mm. in diameter, and reaches nearly to the bottom of a 4-litre bottle, which serves as a receiver. The iron plate upon which the collar rests is heated with a large Meker burner, and to avoid loss of heat, the tripod is surrounded by sheets of asbestos board. The duration of each distillation is further shortened by covering the upper part of the flask with an asbestos jacket. This jacket is made by first covering that part of the flask which projects above the collar with a layer of moist filter paper. Asbestos felt which been soaked in water is then laid upon the paper in overlapping pieces and smoothed down to an even continuous layer. Wet asbestos cement is then laid over the whole exterior of the jacket. The opening in the top of the jacket is made sufficiently large to permit of the removal of the cap from the flask. The cap is allowed to dry on the flask and is then removed, and its lower edge and the upper rim are dipped in a solution of sodium silicate to stiffen them. The receiver stands in an earthenware jar.

*Distillation.*

One kilogrm. of the crude zinc oxide is introduced into the flask, water is placed in the receiver to such depth as just to cover the end of the glass tube, and the earthenware jar in which the bottle stands is filled with cracked ice. 2500 cc. of commercial concentrated hydrochloric acid (1 : 18 sp. gr.) is next driven into the flask through the glass tube in the stopper, and the tube is then replaced by a solid glass plug. The heating of the flask is begun and continued until 2000 cc. of the distillate has collected, this amount having been shown spectroscopically to suffice for the recovery of all the germanium. The flask is then disconnected from the condenser, and the inner tube of the condenser and the tube attached to its far end are rinsed out into the receiver with a little concentrated hydrochloric acid. At the end of the distillation the material in the receiver is a turbid liquid consisting essentially of hydrochloric acid carrying germanium and arsenic in solution. The duration of a distillation is usually from three to five hours. In this laboratory the stills were set up in pairs, and at one time twenty such stills were in simultaneous operation.

*The Precipitation of Germanium and Arsenic by Hydrogen Sulphide.*

The acid distillate may now be precipitated by hydrogen sulphide in such manner as to throw down all of the arsenic and germanium that are present, or the conditions may be so regulated as to cause the precipitation of arsenic trisulphide alone or mixed with only a very small amount of germanium sulphide. This last procedure was used by Winkler (*J. f. prakt. Chem.*, 1886, cxlii., 194), and is now being studied in this laboratory.

The method that we have employed up to the present time involves the simultaneous precipitation of the sulphides of germanium and arsenic.

Successive distillates are poured into a 15-litre glass bottle until about 10 litres of the solution has been collected. Since the precipitation of germanium disulphide is most complete when the acid concentration is about 6N, concentrated sulphuric acid is slowly added to the contents of the bottle until the acidity is brought to about this point. The acid is run in from a separatory funnel that passes through one opening of a two-hole rubber stopper inserted in the neck of the bottle. A short, bent, delivery tube is placed in the other opening of the stopper, and this tube dips into a litre of 6N sulphuric acid that has been saturated with hydrogen sulphide. This serves to stop any germanium tetrachloride that might be volatilised during the addition of the sulphuric acid. Washed hydrogen sulphide is now passed through this solution Yellow sulphide of arsenic tinct layer on the top of the yellow sulphide of is first precipitated. White germanium disulphide next appears, and if the liquid is not agitated, this white sulphide separates as a distinct layer on the top of the yellow sulphide of arsenic When precipitation is complete, the large bottle is stoppered and is allowed to stand for 24 hours. The contents of the bottle is then brought upon a filter and the sulphides are washed with the aid of suction with 3N sulphuric acid that has been saturated with hydrogen sulphide.

The filtrate from the sulphides of germanium and arsenic is placed in a large bottle or in a tall, covered, glass cylinder, and allowed to stand for 48 hours. At the end of this time a slight precipitate of the sulphides separates out. The supernatant liquid is then syphoned off and the bottle or cylinder is filled with the filtrate from the next precipitation, which is again allowed to stand for 48 hours. When a fairly large amount of the sulphides has accumulated in the vessel, it is brought upon a filter and washed as before. The amount of germanium that is recovered by this treatment averages about 2 mgrms. for every litre of filtrate.

From this point forward, two different procedures have been followed. In the first of these the moist sulphides are dissolved in a 50 per cent solution of sodium hydroxide with the aid of heat. Successive portions of the sulphides are added to this solution until a small amount is left undissolved. This is then taken into solution by the addition of a little more of the concentrated solution of sodium hydroxide, and then about 8 grms. of solid sodium hydroxide is added to render the solution strongly alkaline, which facilitates the later oxidation of the arsenic. This solution is then placed in a Pyrex flask, which is provided with a rubber stopper that carries a delivery tube, a separatory funnel, and a glass tube that reaches nearly to the bottom of the flask. This last tube has a wider tube fused to its lower end to avoid stoppage. The flask is placed on an asbestos collar, and is connected with a condenser and a receiver in the manner above described. Washed chlorine is then passed through the liquid in the flask to convert the arsenic to the pentavalent form. When the contents of the flask has been saturated with chlorine, and the apparatus is filled with the gas, the speed of the flow of chlorine is lessened, and concentrated hydrochloric acid is run into the flask through the separatory funnel until the acid is in large excess. The flask is then heated and the germanium tetrachloride is distilled in a slow current of chlorine, the distillation being continued until half of the liquid in the flask has passed over.

The major part of the germanium tetrachloride passes over between 90° and 100°. If the tetrachloride is present in appreciable amount, it will appear in the inner tube of the condenser in oily drops. Instead of collecting the germanium tetrachloride as such from this distillation, some water is placed in the receiver to hydrolyze the compound. The resulting hydrated germanium dioxide is pure white in colour. If any of the oily tertrachloride is seen to collect under the layer of liquid on the bottom of the receiver during the distillation, it is an indication that the concentration of hydrochloric acid in the receiver is so high as to repress the hydrolysis of the germanium tetrachloride. In such case more water is poured into the receiver When half of the liquid in the flask has passed over, the receiver is removed and a fresh receiver containing some water is put in its place. A volume of concentrated hydrochloric acid, equal to the volume of the liquid that has distilled over is now run into the flask through the separatory funnel, and the distillation is continued. When half of the liquid now in the flask is distilled over, most of the germanium tetrachloride has usually passed into the distillate, but it was found that complete separation of that element as the tetrachloride is effected only by many repetitions of the distillation.

The hydrated germanium dioxide is now collected on a small disc of filter paper supported by a Witt plate in a large funnel and is washed first with dilute sulphuric acid and then with small portions of cold water. It is transferred to an evaporating dish and is dried in an air bath at a temperature of 110°. Photographs of the arc spectra of various portions of this material showed that the germanium dioxide contained traces of sodium, calcium, and iron. Fractional precipitation of a solution of a sample of the dioxide by hydrogen sulphide failed to disclose the presence of arsenic.

Germanium in the filtrate and washings from the hydrolysed germanium dioxide is recovered by precipitation with hydrogen sulphide and set aside for 24 hours. The white germanium disulphide is collected on a filter disc, and is washed with 3N sulphuric acid that has been saturated with hydrogen sulphide. The precipitate is then transferred to an evaporating dish, is moistened with nitric acid (1 : 1), is heated until almost all of the nitric acid has been removed, is again moistened with concentrated nitric acid and heated, and is finally ignited in a crucible. When a fairly large amount of germanium dioxide has thus been recovered from the filtrate and wash water, it is again distilled in chlorine to complete its purification.

To free the germanium dioxide from the traces of impurities noted above, it is dissolved in a slight excess of sodium hydroxide with the aid of heat, the solution is treated with chlorine in the manner above described, hydrochloric acid is

added, and the germanium tetrachloride is again distilled off in a current of chlorine and is hydrolysed as before.

The above method for the separation of germanium and arsenic gives quite satisfactory results in respect to the completeness of the recovery of the germanium, but it is open to the following objections.

The precipitate of the mixed sulphides contains a preponderating amount of arsenious sulphide This necessitates the use of large quantities of sodium hydroxide, chlorine, and hydrochloric acid, and greatly lengthens the time of treatment with chlorine. Again, the addition of hydrochloric acid to the chlorinated solution of the mixed sulphides in sodium hydroxide reprecipitates a part of the sulphides, and the conversion of the germanium in this precipitate into the volatile germanium tetrachloride by the action of hydrochloric acid and chlorine proceeds very slowly. Furthermore, a large amount of arsenic in the precipitate causes the appearance of some of that element in the distillate even though the current of chlorine through the apparatus is not interrupted during the distillation. This fact necessitates a second precipitation of the sulphides of germanium and arsenic and a redistillation in chlorine in order to free the germanium completely from arsenic.

It is evident that these difficulties would largely be obviated if the greater part of the arsenic could be separated from the germanium before the distillation in chlorine. Preliminary experiments indicated that this separation could be accomplished by roasting the dried sulphides in air, and this led to the development of the second procedure for the treatment of the mixed sulphides, which is as follows:—

If the mixed sulphides of germanium and arsenic are to be roasted, it is, of course, essential that the sulphide precipitate be washed free from chlorides before the roasting to avoid loss of germanium through volatilisation of germanium tetrachloride. To this end the washing of the sulphides with 3N sulphuric acid is continued until the chlorides are completely removed. The absence of chlorides in the wash water is ascertained by adding cadmium nitrate to a portion of the liquid to precipitate the hydrogen sulphide, filtering off the precipitate, and then adding silver nitrate to the filtrate. The washed sulphides are transferred to a large evaporating dish and are dried in an air bath at 110°.

The dried sulphides consist of from 78 to 90 per cent of arsenious sulphide, the remainder being germanium disulphide and moisture, together with small quantities of sulphur and sulphuric acid. These dry, crude sulphides are placed in shallow iron dishes, and are roasted in a muffle furnace at a temperature not to exceed 500°. This removes the greater part of the arsenic. In the roasting of the sulphides, it is important that the temperature does not rise above 500°, for otherwise there will be a loss of germanium. When the roasting was carried on at a temperature somewhat above 600°, about 30 per cent of the germanium was volatilised. At temperatures ranging between 800° and 900°, about 90 per cent of the germanium was lost by volatilisation. That there was no loss of germanium when the roasting was carried on at a temperature not above 500° was ascertained by placing a curved sheet of aluminium above the iron dish in the muffle and subjecting to spectrographic examination the sublimate that collected on it. The roasting is stopped when fumes cease to appear.

Each of three 100-grm. samples of the dried, crude sulphides yielded, on roasting, about 24 grms. of the germaniferous residue. The actual decrease in the amount of arsenic was, however, greater than this difference of weight indicates, because of the formation of a considerable amount of iron oxide during the roasting. The extent of the removal of arsenic was approximately ascertained by determining the amount of arsenic in an unroasted sample and in that sample after roasting. Before roasting, the material contained 78·2 per cent of $As_2S_3$, and after roasting, 5·52 per cent of arsenic calculated as $As_2S_3$. These results indicate that somewhat over 90 per cent of the arsenic is removed by this treatment.

The germanium in this residue is extracted by dissolving the finely pulverised material in a 50 per cent solution of sodium hydroxide with the aid of heat. The heating is then stopped and the flask is connected with a condenser and receiver for distillation in the manner previously described. Chlorine is passed through the apparatus until the liquid in the flask is saturated, whereupon the speed of flow of the chlorine is lessened and two parts by weight of concentrated hydrochloric acid to every one part by weight of the roasted residue is next run into the flask through the separatory funnel Half of the liquid in the flask is distilled over and then an equal volume of concentrated hydrochloric acid is run into the flask and that same volume of distillate is again collected. This usually completely removes the germanium and no more than faint traces of arsenic are found in the distillate. The resulting hydrated germanium dioxide is freed from the last traces of arsenic by dissolving it in sodium hydroxide, chlorinating the solution, and again distilling with hydrochloric acid in a current of chlorine.

This procedure of first roasting the mixed sulphides to remove the greater part of the arsenic and then distilling off the germanium tetrachloride from the residue is superior to the first method of distilling the germanium tetrachloride from the mixed sulphides direct, in that the consumption of materials is less, the time needed for the distillation is much shorter, and the separation from arsenic is more complete. It possesses, however, one drawback, the necessity of washing the mixed sulphides free from chlorides before roasting. If a small sample of the sulphides be washed with 3N sulphuric acid that has been saturated with hydrogen sulphide, chlorides can be removed quite completely and the filtrate is free from detectable amounts of germanium, but it was found that when this method was used on a large scale, repeated washing with 3N sulphuric acid yields eventually a milky filtrate which slowly deposits white germanium sulphide when its acidity is brought up to 6N. 5N sulphuric acid saturated with hydrogen sulphide was substituted for the 3N acid. This gave a clear filtrate from which no appreciable amount of germanium sulphide separated on standing, but the removal of the chlorides was very slow. Attempts to wash the

precipitated sulphides with 5N sulphuric acid by decantation led to no satisfactory results.

Either of the above processes yields a very pure germanium dioxide. The first gives a somewhat higher yield, and the second procedure is considerably shorter. The precipitation of arsenic trisulphide substantially free from germanium sulphide from weakly acid solutions is now being studied in the hope that a procedure superior to either of those above described may be developed.

(To be continued).

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences.* Vol. clxxiii., No. 11.

"Induction Spectrum of Rubidium."—By M. Louis Dunoyer.

"The Inversion of Rotatory Power of Derivatives of Tartaric Acid."—By M. R. de Mallemann.

"Influence of Temperature on the Utilisation of Glucose for the Development of Aspergillus Niger."—By MM. Emile F. Terroime and René Durmser.

## NOTES.

The *Fuel Economy Review* for August contains an important paper on the "Economics of Coal Production," by Prof. Henry Louis, M.A., D.Sc., A.R.S.M. The writer takes a very serious view of the present situation in the coal industry, and gives much valuable statistical information. With regard to the decrease in production in the coal industry, it is stated that "it is becoming increasingly evident that unless work is to be done in the future in a different spirit to what it has been in the past, the British coal industry is doomed to disappear." This is a statement of very serious import, and it is to be hoped that the different spirit that many are hoping for will soon influence both colliery owners and miners. Contrasted with other countries, British coal costs much more to produce, and we are at the moment surrounded by competitors more favourably circumstanced than we are, a condition that does not seem very hopeful. Our only chance for holding our own is that of greatly increased production, which is quite possible provided the hoped for "new spirit" will come along. Prof. Louis's final conclusion is that an increase in production with a corresponding decrease in selling price is the only means of stimulating the demand and reviving trade, and the essential condition to render this possible is the cheapening of the coal supply. In coal production as in all other branches of our national industries, our needs may be summed up in one phrase: Less "Labour" and more Work!

## NEW COMPANIES.

The under-mentioned particulars of New Companies recently registered are taken from the Daily Register compiled by Jordan & Sons, Limited, Company Registration Agents, Chancery Lane, W.C.2.

Vitamines, Limited.—(176740)—Registered September 10th, 1921. To acquire Patents and to Manufacture, Deal in, or otherwise turn to account, Food of all descriptions. Nominal Capital: £1,000 in 20,000 Shares of 1/- each. Directors: E. Ogdew, Belsfield, South Shore, Blackpool; Isabella C. Morgan, 7, Park Street, Swinton. Qualification of Directors: 1 Share Remuneration of Directors. To be voted by Company in General Meeting

W. Dalby, Limited.—(177641)—Registered September 10th, 1921. 167, Charnwood Street, Leicester. To carry on the business of Chemists and Druggists. Nominal Capital: £1,000 in 1,000 Ordinary Shares of £1 each. Directors: W. Dalby, 167, Charnwood Street, Leicester K. C. Biggs, 51, Highfield Street, Leicester. Qualification of Directors · 1 Share. Remuneration of Directors. To be voted by Company in General Meeting.

Industrial Soap, Co., Limited.—176784)—Registered September 14th, 1921. To carry on the business of Manufacturers and Dealers in Soap, Oils and Oleaginous and Saponaceous substances Nominal Capital: £10,000 in 10,000 Shares of £1 each. Directors To be appointed by Subscribers. Qualification of Directors: £100. Remuneration of Directors: To be voted by Company in General Meeting. Subscribers: W. Nichol, 2, Victoria Road, Levenshulme (500 Shares); C. Miller, 41, Albert Road, Levenshulme (500 Shares), J. Miller, Green Mount, 220a, Plymouth Grove, Chorlton-on-Meadlock (500 Shares); F. Bridge, Smithfield Market, Manchester (500 Shares); G. Marsdenam, 8, Market Street, Warrington (300 Shares); H. W. Billam, 7, St. John Street, Manchester (400 Shares).

Fletcher's Pharmacy, Limited.—(176749)—Registered September 12th, 1921. 166-168, North Street, Leeds. To carry on the business of Chemists and Druggists. Nominal Capital £500 in 500 Shares of £1 each Directors: P. Hipps, 50, Kent Road, Harrogate; M. Fletcher, 166-168, North Street, Leeds. Qualification of Directors · 50 Shares. Remuneration of Directors · To be voted by Company.

Harris & Morris (Chemists), Limited.—(176734)—Registered September 10th, 1921. 199a, High Street, Swansea To carry on the business of Chemists and Druggists. Nominal Capital £500 in 500 Shares of £1 each. Directors: To be appointed by Subscribers. Qualification of Directors: 1 Share. Remuneration of Directors: To be voted by Company.

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# BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

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## NOTES ON WATER POWER DEVELOPMENT.

ADDRESS DELIVERED BEFORE SECTION G (ENGINEERING)

By PROFESSOR A. H. GIBSON, D.Sc., President of the Section.

THE extent to which the water powers of the world have been investigated and developed during the past decade forms one of the striking engineering features of the period. Although falling or flowing water formed the earliest of the natural sources of energy to be utilised for industrial purposes, it is of interest to note that two-thirds of the water power at present in use has been developed within the last ten years.

The reasons for the revival of interest in this question are partly technical and partly economic. The technical development of electric generation and transmission has made it economically possible to utilise powers remote from any industrial centre, while a rapid increase in the demand for energy for general industrial purposes and for the many electro-chemical, electro-physical, and electro-metallurgical processes which are now in general use, and whose field is rapidly growing, has provided a ready outlet for all such energy as could be cheaply developed.

The urgent demand for energy to supply the abnormal requirements of the war period, combined with the world shortage of fuel, was responsible for an unprecedented rate of development in most countries with available water power resources, and especially in those countries normally dependent on imported fuel.

Thus in France some 850,000 water horse-power has been put into commission since 1915, and the country now has 1,600,000 horse-power under control as compared with 750,000 before the war. In Switzerland some 600,000 horse-power has been developed since 1914, or is in course of construction, as compared with 880,000 horse-power before the war. In Spain, where the pre-war output was 150,000 horse-power, the present output is 620,000 horse-power, and about 260,000 horse-power is now in course of development, while the Spanish Ministerio de Fomento is considering the development of some 2,000,000 horse-power to be delivered into a network of transmission lines covering the industrial parts of the country.

In Italy, schemes totalling about 300,000 horse-power are under way, and it is estimated that the total output will shortly amount to 2,000,000 horse-power. The Government Hydrographical Department is now engaged in gauging and surveying the profiles of the principal rivers, and statistics of available reservoir sites of lakes suitable for storage and of available horse-power are being compiled.

Japan, which only recently began to investigate her water powers, has, since 1916, developed over 1,000,000 horse-power, or almost 20 per cent of her available resources.

In Canada and the United States many large schemes have recently been brought into service, and some extremely large installations are now in course of construction or are projected. Thus the Queenston-Chippewa project on the Canadian side of the Niagara River is intended to develop some 500,000 horse-power, while a projected development of the St. Lawrence River will be capable of yielding 1,700,000 horse-power. In Canada, the total development (2·3 million horse-power) in 1918 was almost three times as great as in 1910. In the United States of America the development has increased from something under two million horse-power in 1901, to 5·3 millions in 1908, and to nearly 10·0 millions in 1920.

Rapid as has been the development of water power in the United States in the past, it has been retarded by the fact that the privilege of using the national forests or other public lands for water power development has only been granted by the issuing of permits which were not available for any definite period and which were revocable at the will of the Granting Authority. In the case of development on navigable streams, hwether on public or private land, each scheme has required a special Act of Congress, and these Acts could be revoked by Congress at any time. Owing to the uncertainty of tenure there has naturally been some reluctance to invest capital in such undertakings.

By the recent Federal Water Power Act, signed in June, 1920, licences for such developments may now be issued under the jurisdiction of a new body, known as the Federal Power Commission, for a period not exceeding 50 years, at the end of which the licence may be renewed, or the Government may take over the enterprise upon compensation of the licensee. In the issuing of licences, preference is to be given to State and municipal applications. The effect of this Act may be inferred from the fact that, within a month of its being signed, applications for licences to develop over 500,000 horse-power had been filed. The duty of collecting, recording, and publishing data regarding the utilisation of water resources, the water-power industry and its relation to other industries, and regarding the capacity, development costs, and relationship to possible markets, of power sites, has also been assigned to this Federal Power Commission.

*World's Available Water Power.*—During the past few years much attention has been paid to statistics of available and developed water powers. In the case of developed powers, these are usually stated in terms of the capacity of the installed machinery. This machinery is in general only used to its full capacity over a portion of each day, although in many such cases water is available for providing continuous power if desired.

Estimates of potential power are always to be accepted with considerable reserve. In order to make a reasonably accurate estimate, the run off from the catchment area and the variation in this run off from month to month and from year to

year, must be known, and it is only in comparatively rare cases that this information is as yet available. Moreover, there is as yet no standard basis on which potential power is computed.

The power available from a given stream during the wet season is many times as great as during the dry season, unless sufficient storage is available to equalise the flow throughout the year, and the cost of such storage would in general be prohibitive, even if it were physically possible to provide it.

The United States Geological Survey takes the maximum useful flow of a stream as being that which may be guaranteed during six months in each year. The minimum flow is taken as the average which can be guaranteed over the two driest consecutive seven-day periods in each year, along with the additional flow which may be obtained during this period by developing any available storage capacity in the upper waters of the stream Estimates of potential power based on storage capacity are, however, subject to a wide margin of error owing to the limited data available, and in the following table the potential water-power is estimated on the basis of the maximum flow as just defined, and in terms of continuous 24-hour power.

Millions of Horse Power.

| | Available | Developed |
|---|---|---|
| Great Britain | 0·9 | 0·2 |
| Canada | 23·0 | 3·28* |
| Remainder of British Empire, including: Australia, Africa (East), Africa (South), Africa (West), British Guiana, India and Ceylon, New Zealand, Papua | 30·0 to 50·0 | 0·7 |
| Austria | 6·5 | 0·57 |
| Brazil | 26·0 | 0·32 |
| Dutch East Indies | 5·5 | — |
| France | 5·6 | 1·6 |
| Germany | 1·5 | 0·75 |
| Iceland | 4·0 | 1·0† |
| Italy | 4·0 | 1·25 |
| Japan | 8·0 | 1·5 |
| Norway | 7·5 | 1·25 |
| Russia | 20·0 | 1·0 |
| Spain | 5·0 | 0·88 |
| Sweden | 6·2 | 1·2 |
| Switzerland | 4·0 | 1·4 |
| United States of America | 28·0 | 9·8 |

* Including projected extensions to plants now in operation.

† Projected but not yet constructed.

Adopting these figures, it appears that the available horse-power of the world is of the order of 200 millions, of which approximately 25 millions is at present developed or is in course of development.

*Power Available in Great Britain and in the British Empire.*—With the noteworthy exceptions of Canada and New Zealand, practically nothing had been done, prior to 1915, by any part of the British Empire to develop or even systematically to investigate the possibilities of developing its water powers. It is true that a number of large installations had been constructed in India and Tasmania, but their aggregate output was relatively inconsiderable.

Since then, however, there has been a general tendency to initiate such investigations, and at the present time these are being carried out with varying degrees of thoroughness in India, Ceylon, Australia, South and East Africa, and British Guiana. While it is known that there is ample water-power in Newfoundland, Nigeria, Rhodesia, Papua, and the Gold Coast, no very definite information is available, nor are any steps apparenly being taken to obtain data in these countries.

The Water-power Committee of the Conjoint Board of Scientific Societies, which has been studying the state of investigation and development throughout the Empire since 1917, has, however, come to the conclusion that its total available water-power resources are at least equivalent to between 50 and 70 million horse-power.

Of the developed power in the Empire about 80 per cent is in Canada. Throughout the remainder of its territories only about 700,000 horse-power is as yet developed, or only a little over 1 per cent of the power available, a figure which compares with about 24 per cent for the whole of Europe, and 21 per cent for North America, including Canada and the U.S.A. These figures sufficiently indicate the relatively large scope for future development.

*Power Available in Great Britain.*—With a view of ascertaining the resources of our own islands, a Board of Trade Water Power Resources Committee was appointed in 1918. This Committee, which has just presented its final report, has carried out preliminary surveys of as many of the more promising sites as its limited funds allowed, and has obtained data from the Board of Agriculture for Scotland, the Ordnance Survey Department, the Ministry of Munitions, and from civil engineers in private practice, regarding a large number of other sites.

As might be anticipated, Scotland, with its comparatively high rainfall, mountainous area, and natural lochs, possesses relatively greater possibilities than the remainder of the United Kingdom, and investigation has shown that it offers a number of comparatively large schemes. Nine of the more immediately promising of those examined by the Committee have an average output ranging from 7,000 to 40,000 continuous 24-hour horse-power, and an aggregate capacity of 183,000 horse-power, while in every case the estimated cost of construction is such that power could be developed at a cost appreciably less than from a coal-fired station built and operated under present-day conditions. The aggregate output of the Scottish schemes brought before the notice of the Committee, some of which, however, are not commercially feasible at the moment, is roughly 270,000 continuous horse-power.

In addition to these there are a very large number of other small schemes which have not yet been investigated,* and it is probably well within the mark to say that there are water-power sites in the country capable of developing the equivalent of 400,000 continuous horse-power or 1,500,000

*In a paper read before the Royal Society of Arts on January 25, 1918, Mr. A Newlands, M.I.C.E., gave a list of 122 potential Scottish schemes, the capacity of which he estimated, on a very conservative basis, at 375,000 horse-power.

horse-power over a normal working week, at least as cheaply as from a coal-fired installation.

A number of attractive schemes are also available in North Wales, though these are in general more expensive than those in Scotland

Owing to the general flatness of the gradients, there are, except possibly around Dartmoor, no schemes of any large individual magnitude in England, but there are a large number of powers ranging from 100 to 1,000 horse-power which might be developed from river flow uncontrolled by storage.

Investigations on a few typical watersheds throughout England and Wales appear to show that the possible output averages approximately eight continuous horse-power per square mile of catchment area, which would be equivalent to an aggregate of about 450,000 horse-power. Although much of this potential output is not commercially feasible, it would give the equivalent of 500,000 horse-power over a normal working week if only 30 per cent of it were fully utilised.

In the report recently issued by the Irish Sub-Committee of the Board of Trade Water Power Committee, it is estimated that approximately 500,000 continuous 24-hour horse-power is commercially available in Ireland, and that if utilised over a 48-hour working week, its capacity would be at least seven times as great as that of the engine power at present installed in the country for industrial purposes.

It appears then that, although the water-power possibilities of the United Kingdom are small in comparison with those of some more favoured countries, they are by no means so negligible as is commonly supposed, even in comparison with the present industrial steam power resources of the country.

The capacity of the fuel power plants installed for industrial and public utility services in the United Kingdom in 1907 was approximately 9·8 million horse-power. Allowing for an increase of 15 per cent since then, and an average load factor of 35 per cent, this is equivalent to 32,000 million horse-power hours per annum, or to a continuous 24-hour output of only 3·7 million horse-power.

According to Sir Dugald Clerk, the average consumption of coal per horse-power hour in this country is about 3·9lb., which, on the above basis, would involve a total annual consumption of 55 million tons for industrial purposes, not including railways or steamships. This figure is in substantial agreement with the estimate of 60 million tons made for factory consumption in 1913 by the Coal Conservation Committee of the Ministry of Reconstruction, since this latter figure also includes coal used for heating and other manufacturing processes in factories.

Adopting this figure of 32,000 million horse-power hours as the annual demand for power for industrial purposes, it appears that the inland water-power resources of the United Kingdom are capable of supplying about 27 per cent of this, a proportion which, in such an industrial country as our own, is somewhat surprisingly large.

Many of the small powers would be well adapted for linking up, as automatic or semi-automatic stations, into a general network of electricity supply, or for augmenting the output of municipal supply works, as has been done so successfully, for example, at Chester, Worcester, and Salisbury.

The development of the many small schemes available in the Scottish Highlands would probably have a great effect on the social life of the community. It would go far towards reviving and extending those small local industries which should form an essential feature of the ideal rural township. Commercially such undertakings may appear to be of small importance, but as a factor in promoting the welfare of the State, economical and political, their influence can hardly be over-estimated.

Some of the larger schemes in Scotland would lend themselves admirably to transmission to its industrial districts, while others, in close vicinity to the sea-board, would appear to be well adapted for supplying chemical, or electro-physical, or metallurgical processes

There is a probability that at least two of these schemes will be developed in the near future. One of these—the Lochaber scheme—is capable of developing some 72,000 continuous horse-power, which is to be utilised largely in the manufacture of aluminium. It is interesting to note that when this scheme is completed the British Aluminium Corporation will have, with their station at Kinlochleven, an average continuous output of over 100,000 horse-power, and a maximum capacity of almost 140,000 horse-power.

The second—the scheme of the Grampian Power Company—is intended ultimately to develop upwards of 40,000 continuous horse-power, which it is proposed to use largely for general industrial purposes.

Should this latter scheme be carried to a successful conclusion it is likely to give an impetus to large-scale water-power development in Scotland. Its successful operation would certainly lead to the development of others of the same type, which would help to provide a much-needed home training ground for British hydro-electric engineers.

While this is admittedly an inopportune moment to suggest anything in the nature of State co-operation in such developments, it may be pointed out that many of the Scottish powers in particular occur in sparsely-populated districts, and that, although they would ultimately become remunerative, the difficulty of raising the capital necessary for their development is great. In view of their direct and indirect advantage to the community it would appear not unreasonable to advocate that financial assistance should be granted by the State in the earlier stages of such developments. If such assistance, say, in the form of a loan maturing after a period of 10 or 15 years, could be granted, it would certainly give an immediate impetus to the development of water-power in this country.

*Conservation.*—The importance of water-power development from the point of view of conservation of natural resources requires no emphasis. When the value of coal purely as a chemical asset or as a factor in the manufacture of such materials as iron and steel, cement, &c., is considered, its use as a fuel for power purposes, when any other equally cheap source of energy is available, would appear, indeed, to be unjustifiable.

The consumption of coal in the best modern

steam plant of large size, giving continuous output, would be about nine tons per horse-power year, and on this basis the world's available water-power if utilised would be equivalent to some 1,800,000,000 tons of coal per annum. The world's output of coal in 1913 was approximately 1,200,000,000 tons, of which about 500,000,000 were used for industrial power purposes, so that on this basis 55,000 000 continuous water horse-power would be equivalent to the world's industrial energy at that date.

Not only does the use of water power lead to a direct conservation of fuel resources, but it also serves to a notable degree to conserve man-power. To take an extreme example, each of the 40,000 horse-power units now being installed at Niagara Falls will require for operation two men per shift. It is estimated that to produce the same power from a series of small factory steam plants, over 800 men would be required to mine, hoist, screen, load, transport by rail, unload, and fire under boilers the coal required, while, if account be taken of the additional labour involved in horse transport, wear and tear of roads and of railroad tracks and rolling stock, the number would be considerably increased.

*Uses of Hydro-Electric Energy.*—While a large proportion of the energy developed from water-power is utilised for industrial purposes and for lighting, power, and traction, an increasing proportion is being used for electro-chemical and electro-metallurgical processes. It is probable, indeed, that we are only on the threshold of developments in electro-chemistry, and that the future demand for energy for such processes will be extremely large.

In Norway the electro-chemical industry absorbed 770,000 horse-power in 1918, or approximately 75 per cent of the total output, as compared with 1,500 horse-power in 1910. Of this, some 400,000 horse-power was utilised in nitrogen fixation alone.

The production of electric steel in the U.S.A. increased from 13,700 tons in 1909 to 24,000 tons in 1914, and 511,000 tons in 1918, this latter quantity absorbing 300 million k w. hours, equivalent to almost 400,000 continuous horse-power.

In Canada, in 1918, the pulp and paper industry absorbed 450,000 horse-power, or 20 per cent of the total, while the output of central electric stations amounted to 70 per cent of the total.

The electrification, on a large scale, of trunk line railways is also a probability in the not distant future. In the U.S.A., 650 miles of the main line of the Chicago, Milwaukee, and St. Paul Railway, comprising 850 miles of track, have been electrified, the power for operation being obtained from hydro-electric stations. In France much of the track of the Compagnie du Midi in the region of the Pyrenees has been electrified with the aid of water power; much of the Swiss railway system has been electrified; and the electrification of many other trunk lines on the European continent is at present under consideration.

Quite apart from the probable huge demand in the distant future for energy for the manufacture of artificial fertilisers by some system of nitrogen fixation, agriculture would appear to offer a promising field for the use of hydro-electric power.

Much energy is now being utilised in the U.S.A. for purely agricultural purposes. In California, for example, there is in effect one vast system of electrical supply extending over a distance of 800 miles with 7,200 miles of high-tension transmission lines. This is fed from 75 hydro-electric stations, inter-connected with 47 steam plants, to give a total output of 785,000 horse-power. A further group of 13 hydro-electric schemes now under construction will add another 520,000 horse-power. A large proportion of this power is used in agriculture, and a census in 1915 showed that electric motors, equivalent to over 190,000 horse-power were installed on Californian farms. The Californian rice industry is almost wholly dependent on irrigation made possible by electric pumping, while most of the mechanical processes involved in farming are being performed by electric power.

There can be little doubt that the economic development of many of our tropical dependencies is bound up in the development of their water-power resources. Not only would this enable railroads to be operated, irrigation schemes to be developed, and mineral deposits to be mined and worked, but it would go far to solve the black labour problem, which promises to be one of some difficulty in the near future.

While those outlets for electrical energy which are now in sight promise to absorb all the energy which can be cheaply developed for many years to come, there are many other probable directions in which cheap energy would find a new and profitable outlet. Among these may be mentioned the purification of municipal water supplies; the sterilisation of sewage; the dehydration of food products; and the preservation of timber.

*Scope for Future Water Power Development.*—The figures already quoted indicate that the scope for inland water power development throughout the world, and more particularly throughout the British Empire, is likely to be large for many years to come, and it is gratifying to know that British engineers are prepared to play a large part in such development work.

The utilisation of this water power is likely to give rise to some economic problems of interest and importance When industrial conditions have again become stabilised, the competitive ability of the various nations will depend largely on economy in the application of energy to production and transportation, and the possession of cheap water power is likely largely to counterbalance the possession of such resources as coal and iron as a measure of the industrial capacity of a nation.

While it is probably true in industrial communities that the most attractive water-power schemes have already received attention, many of those available in countries which have hitherto been non-industrial are capable of extremely cheap development and will certainly be utilised as soon as a market for their output can be assured.

It is in such countries that the result of these developments is likely to be most marked, and will require most careful consideration. Thus, the hydro-electric survey of India now being carried out by the Indian Government indicates that very large water power resources are available in the country, and that, although a few large schemes have been or are being developed,

the resources of the country are practically untouched. There can be little doubt that in the course of time a large amount of cheap energy will be available in India for use in industrial processes, and as the country possesses a large and prolific population readily trained to mechanical and industrial processes, along with ample supplies of raw material for many such processes, all the conditions would appear to be favourable for its entry into the rank of manufacturing and industrial nations.

*Modern Tendencies in Water Power Development.*—The large amount of attention which has been concentrated on the various aspects of water power development during the past ten years has been responsible for great modifications and improvements in the design, arrangement, and construction of the plant.

Broadly speaking, these have been in the direction of increasing the size, capacity, reliability, and efficiency of individual units; of improvng the design of the turbine setting and of the head and tail works; of increasing the rotative speed of low head turbines; of detailed modifications in the reaction type of turbine to enable it to operate under higher heads than have hitherto been considered feasible; and of increasing the voltage utilised in transmission.

The capacity of individual units has been increased rapidly during recent years, and at the present time units having a maximum capacity of 55,000 horse-power under a head of 305ft. are being installed in the Queenston-Chippewa project at Niagara, while units of 100,000 horse-power are projected for an extension of the same plant.

These modern high-power turbines are usually of the vertical shaft, single runner type, with the weight of the shaft, runner, and generator carried from a single thrust bearing of the Michell type. This type lends itself to a simple and efficient form of setting, while the friction losses in the turbine are extremely low. As a result of careful overall design it has been found possible to build units of this type having an efficiency of approximately 93 per cent.

One of the great drawbacks of the low head turbine in the past has been its relatively slow speed of rotation, which necessitated either a slow speed, and consequently costly generator, or expensive gearing As a result of experiment it has, however, been possible so to modify the form of the runner as greatly to increase the speed of rotation under a given head without seriously reducing the efficiency.

Investigations in this direction are still in progress and promise to give rise to important results. At the present time, however, turbines are in existence which are capable of working efficiently at speeds at least five times as great as would have been thought feasible ten years ago.

The non-provision of a suitable pipe line has, until recent years, tended to retard the development of plants for very high heads. Under such heads the necessary wall thickness, even with a moderate pipe diameter, becomes too great to permit of the use of riveted joints. Recent developments in electric welding and oxy-acetylene welding have, however, rendered it possible to construct suitable welded pipes, and by their aid, and by the use of solid drawn steel pipes in extreme cases, it has been found possible to harness some very high falls. The highest as yet utilised is at the Fully installation in Switzerland. Here the working head is 5,412ft., corresponding to a working pressure of 2,360lb. square inch. The pipe line is 19·7in. in diameter, and 1¾in. thick at its lower end, and each of the three Pelton wheels in the power house develops 3,000 horse-power, with an efficiency of 82 per cent.

Until comparatively recently the Pelton wheel was looked upon as the only practicable turbine for high heads, and the use of the Francis turbine was restricted to heads below about 400ft. This was due partly to the fact that a reaction turbine of comparatively small dimensions gives a large output under a high head, and except in turbines of comparatively large power the water passages become very small, and the friction losses in consequence large.

A further and more important reason for the general choice of the Pelton wheel for high heads was the fact that in the earlier Francis turbines, when operating under heads involving high speeds of water flow, corrosion of the runner was very serious. This corrosion is now generally attributed to the liberation of air containing nascent oxygen, at points where eddy formation causes regions of low pressure. Careful design of the vanes has enabled this to be largely prevented in modern runners, and in consequence the field of useful application of the Francis turbine has been extended until at present turbines of this type are operating successfully under a head of 850ft., and this limit will probably be exceeded in the near future.

The great increase in all constructional costs, since 1914 has increased the cost of the average hydro-electric plant by something of the order of 150 per cent., and since the cost of energy produced by such a plant is mainly due to fixed charges on the capital expenditure, this cost has gone up in an even greater proportion owing to the higher interest charges now demanded.

It is true that the same increased cost applies within narrow limits to the output from every steam plant erected since the War, and the relative position of the two types of power plant with coal at about 25s. per ton is much the same as before the war.

The fact remains, however, that a newly-constructed hydro-electric plant has often to compete in the market with a steam plant built in pre-war whose standing charges are comparatively low, and in order to enable it to do so with success the constructional cost must often be reduced to a minimum compatible with safe and efficient operation. With this in view, many modifications in design and construction have been introduced in recent plants, but there would still appear to be ample scope for investigation into the possibility of reducing the first cost by modifying many of the details of design and methods of construction now in common use.

Among recent modifications in this direction may be mentioned :—

(1) The elimination of the dam in storage schemes in which natural lochs or reservoirs are utilised, this water level being drawn down in times of drought instead of being raised in times of flood. This

reduces the cost of construction appreciably in favourable circumstances, and eliminates the necessity for paying compensation for flooding of the land surrounding the reservoir.

(2) The substitution, where feasible, of rockfill dams for those of masonry or monolithic concrete.

(3) The introduction of outdoor installations with the minimum of power house construction.

(4) The simplification of the power plant.

Some progress has already been made in these directions, and it is probable that experience based on recent installations and experimental investigations will enable considerable further progress to be made.

*Research in Hydro-Electric Problems.*—There are few branches of engineering in which research is more urgently required and in which it might be more directly useful.

Among the many questions still requiring investigation on the civil and mechanical side may be mentioned :—

(1) *Turbines.*—Investigation of turbine corrosion as affected by the material and shape of the vanes.

Effect of erosion due to sand and silt.

Resistance to erosion offered by different materials and coatings.

Bucket design in low head high-speed turbines.

Draft tube design.

Investigation of the directions and velocities of flow in modern types of high-speed turbines.

Investigation of the degree of guidance as affected by the number of guide and runner vanes.

(2) *Conduits and Pressure Tunnels.*—The design of large pipe lines under low heads with the view of reducing the weight of metal. The investigation of anti-corrosive coatings, so as to reduce the necessity for additional wall thickness to allow for corrosion.

Methods of strengthening large thin-walled pipes against bending and against external pressures.

Methods of lining open canals and of boring and lining pressure tunnels.

Effects of curvature in a canal or tunnel.

(3) *Dams.*—Most efficient methods of construction and best form of section especially for rockfill and earthen dams. Best methods of producing water tightness.

(4) *Run-off Data.*—Since the possibility of designing an installation to develop the available power efficiently and economically depends in many cases essentially on the accuracy of the run-off data available, the possession of acurate data extending over a long series of years is of great value.

While such data may be obtained either from stream gaugings or from rainfall and evaporation records, the former method is by far the more reliable. For a reasonable degree of accuracy, however, records must be available extending over a long period of years, and at the present moment such data is available only in very few cases.

(To be continued)

## GERMANIUM.*

### I.—OCCURRENCE; EXTRACTION FROM GERMANIUM-BEARING ZINC OXIDE; NON-OCCURRENCE IN SAMARSKITE.

By L. M. DENNIS and JACOB PAPISH.

(Concluded from p. 196).

### (*C*) *The Determination of Germanium.*

To gauge the efficiency of the extraction of the germanium from the crude material it was necessary to develop a method for the quantitative determination of germanium. The procedure that was finally adopted is based directly upon the method of extraction that has already been described.

A weighed quantity of the germaniferous zinc oxide that had been dried at 110°, varying in amount from 20 to 100 grms., is ground into a paste with water, and is then poured into a flask that contains a solution of sodium hydroxide. These three substances are used in the proportions of one part of sodium hydroxide, two parts of the crude zinc oxide, and five parts of water The flask is provided with a three-hole rubber stopper, through which are inserted a glass tube that reaches almost to the bottom of the flask, a small Vigreux distilling column, and a small separatory funnel. To the side arm of the Vigreux tube is fused a Liebig condenser, and a glass adapter is fused to the further end of the condenser. The receiver consists of an Erlenmeyer flask that is provided with a two-hole rubber stopper. Through one of these holes passes the glass adapter, which reaches to within a few millimetres of the bottom of the flask. A delivery tube is inserted through the other hole of the stopper, and this tube is connected with a second Erlenmeyer flask. Water is placed in the first Erlenmeyer flask to a depth of 3 cm., and the second flask is half filled with water. The second flask serves as a check upon the completeness of the condensation of germanium chloride in the first receiver. If any germanium is later found to have passed into the second flask, the determination is rejected. Both of the flasks are placed in a trough containing ice water.

In beginning the distillation, a dish containing cracked ice is brought up under the distilling flask and a slow current of washed chlorine is passed into the flask through the glass tube. As soon as the apparatus fills with chlorine, which indicates that the contents of the flask has been saturated with the gas, pure, concentrated hydrochloric acid is slowly introduced through the separatory funnel. The acid that is eventually added is sufficient to neutralize the sodium hydroxide that was originally employed, and in addition, to equal twice the weight of the crude zinc oxide that is being used. The passage of chlorine and the cooling of the flask are continued during the addition of the acid. When all of the acid has been introduced, the dish of cracked ice is replaced by an asbestos collar and the contents of the flask is then heated in the manner already described. When one-half of the liquid has distilled over, an equal volume of concentrated hydro-

*Contribution from the Department of Chemistry of Cornell University. This article is based upon a part of the thesis presented to the Faculty of the Graduate School of Cornell University by Jacob Papish in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

chloric acid is run into the flask and the distillation is continued until half of the liquid has again passed over. The addition of hydrochloric acid and distillation of one-half of the liquid are once more repeated. The heating is then stopped and the two receivers disconnected. Sulphuric acid is added to the contents of each to bring the acidity to 6N, the flasks standing in ice during the addition of the acid. The liquid in each flask is then saturated with hydrogen sulphide, and the flasks are stoppered and set aside for 24 hours. If the passage of the chlorine through the apparatus during the distillation has been slow, and if the receivers have been kept well cooled with ice, no germanium tetrachloride will pass over into the second receiver. A precipitate will, however, appear in the second flask, because of the liberation of sulphur through the interaction of chlorine and hydrogen sulphide. This precipitate is tested spectrographically to ascertain whether it is free from germanium. If it is not, the determination is rejected. The precipitated germanium disulphide in the first flask is brought upon an ashless filter paper and the small amount of precipitate that adheres to the walls of the flask is loosened by means of a rubber "policeman" and brought upon the filter by rinsing with 3N sulphuric acid that has been saturated with hydrogen sulphide. The whole precipitate is now washed with this liquid until the chlorides are removed. The germanium disulphide is then washed with alcohol to remove the sulphuric acid and is next dried. The bulk of the precipitate is removed from the filter and placed in a weighed porcelain crucible. It is is moistened with nitric acid (1 : 1) and the crucible is gently heated until the liquid has been driven off. The crucible is then allowed to cool, and concentrated nitric acid is added. This is also driven off by gentle heating, and the crucible is then heated to dull redness.

Germanium dioxide that has been dried at 110° still contains an appreciable amount of water. Experiments performed in this laboratory by Miss K. M. Tressler, which will be described in a later article, have shown that complete dehydration is secured only when the dioxide is heated to 900°.

The filter paper is incinerated over a second weighed crucible. The product is black, due to the formation of some germanous oxide caused by the reduction of the germanium dioxide by the carbon of the paper. This is oxidised to the dioxide by treatment with nitric acid.

The filtrate from the precipitation of the germanium disulphide is set aside for 48 hours and the precipitate that then appears is treated in the same manner as the first precipitate. The sum of the weight of the dioxide in the two crucibles less the weight of the ash of the two filter papers gives the weight of germanium calculated as dioxide that is present in the original sample.

Although no great accuracy is claimed for the method as thus far developed, two determinations in duplicate of the germanium in different samples of the crude zinc oxide gave concordant results:—

*Sample I.*

| | I | II |
|---|---|---|
| Weight of sample ... | 50 grms. | 75 grms. |
| $GeO_2$ found ... ... | 0·1235 grms. | 0·1860 grms. |
| Per cent $GeO_2$ ... | 0·247 | 0·248 |

*Sample II.*

| | I | II |
|---|---|---|
| Weight of sample ... | 50 grms. | 100 grms. |
| $GeO_2$ found ... ... | 0·0950 grms. | 0·1885 grms. |
| Per cent $GeO_2$ ... | 0·19 | 0·188 |

The completeness of the recovery of germanium from the crude zinc oxide by the method of extraction above described is evidenced by the fact that from a series of runs in which a total of about 10·7 kilogrms. of Sample I. of the undried crude oxide was used, 25·936 grms. of pure $GeO_2$ was obtained.

### *The Non-Occurrence of Germanium in Samarskite.*

Above reference was made to the statement of Khrushchov that he had found germanium in American samarskite. This statement was published in the form of a report in the *Journal of the Russian Physical-Chemical Society.* (We are indebted to the Library of Congress for a pen copy of this report. The translation here given was made by one of us.—J.P.). Literally translated, it reads as follows:—

"K. D. Khrushchov reports about finding germanium in columbium and tantalum minerals. American samarskite was heated in a 300-grm. platinum crucible for the purpose of comminuting the samarskite. After three heatings, the platinum was altered to such an extent that the crucible crumbled to a powder. On dissolving the platinum, a residue was obtained which resembled silica, but it was fairly difficultly soluble in hydrofluoric acid. Assuming the gelatinous sediment to be a germanium dioxide, the reporter found that it was changed very easily by hydrogen to the black powder of germanium. Traces of germanium were also found in tantalite, fergusonite, columbite, gadolinite, and in other minerals. American samarskite contains up to 1·5 per cent germanium. In view of the rarity of argyrodite, the reporter calls attention to samarskite as an important source of germanium."

Lincio (*loc. cit.*) failed to find evidence of the presence of germanium in samarskite. After the method for determining germanium that has been described in the preceding pages had been developed, the question of the occurrence of the element in American samarskite was taken up in this laboratory. 200 grms. of finely-ground selected samarskite was fused with 1200 grms. of primary potassium sulphate. The fused mass was extracted with water, and the residue, which contained a small quantity of undecomposed samarskite, was mixed with more primary potassium sulphate and was fused and extracted with water as before. The two water extracts were combined and were evaporated to dryness.

The insoluble residue from the fusion was moistened with nitric acid, and was then introduced into a Pyrex flask of 500 cc. capacity. 200 cc. of hydrochloric acid was added, and the mixture was subjected to distillation until 150 cc. of distillate had passed over. The distillate was saturated with hydrogen sulphide, and was allowed to stand for 24 hours. The very slight precipitate that formed was collected on a small filter and was dried. The photograph of the arc spectrum of this material failed to show the presence of germanium.

The residue obtained for the water extracts of

the fusion was moistened with nitric acid, and was introduced into a flask of 3-litre capacity. 1500 cc. of concentrated hydrochloric acid was added, and the mixture was distilled until about 600 cc. had passed over. 500 cc of hydrochloric acid was then run into the flask, and a second distillate of 400 cc. was obtainned. The two distillates were united, were saturated with hydrogen sulphide, and were allowed to stand for 24 hours. The slight precipitate that separated showed no spectrographic evidence of the presence of germanium

Khrushchov's report is by no means convincing. He obtained a gelatinous residue which he assumed to be germanium dioxide, but he gives no reasons for this assumption, and it is difficult to imagine what his reasons might have been. The fact that the material was darkened when heated in hydrogen might indicate the presence of a variety of compounds other than germanium dioxide. Moreover, it is probable that when he dissolved the platinum, he used aqua-regia for this purpose. If he did so, all of the germanium would probably have been lost through volatilisation of the germanium tetrachloride. It seems evident, therefore, that Khrushchov's experimental work does not justify his statement that samarskite contains germanium, and the results obtained by Lincio and in this laboratory would seem to show that that mineral does not carry detectable amounts of the element.

*Summary.*

This article contains:—

A brief historical review of the discovery of germanium.

A *resumé* of the published announcements concerning the occurrence of the element.

The details of an experimental study of the extraction of germanium from germanium-bearing zinc oxide, and the preparation of pure germanium dioxide.

Description of a method for the determination of germanium.

The details of an examination of American samarskite which showed that the mineral does not contain germanium in an amount detectable by means of the spectroscope.

Ithaca, N.Y.

## LATENT HEAT OF VAPORISATION.

By J. C. THOMPSON.

THE latent heat of vaporization of a liquid

$$=\frac{P \log_{10} P}{10{\cdot}31 \times D^{\frac{4}{3}}}$$

Where P is the density of the substance compared with its vapour density at boiling point.

Where D is the density of the substance as liquid at its boiling point compared with water at 4°C.

The following table will show thls:—

| Substance | D. | P* | $\frac{P \log P}{10{\cdot}31 \times D^{\frac{4}{3}}}$ | Latent Heat. |
|---|---|---|---|---|
| Water ... | 0·9856 | 1629 | 536·6 | 536·6 |
| Ethyl Ether | 0·736 | 250·2 | 87·58 | 87·4 |
| Benzene ... | 0·82 | 203·5 | 95·21 | 96·1 |
| Oxygen ... | 1·124 | 261 | 52·3 | 52 |

*Calculated from molecular weights and 0·3665 coefficient of expansion of gases from 0 to 100°C. 1000 cc of H = 0·089610 grms.

*Theoretical determination of above Formula.*

Water at 100°C exists in two states the density as liquid being 1629 times the density of gas. The work required to compress a perfect gas from 1 atmosphere to 1629 atmospheres or make its density 1629 times as great is a definite and readily calculated amount. This amount might be expected to bear some relationship to the latent heat of water measured as work Such a relationship does exist, The latent heat multiplied by cube root of the density as liquid is a constant times this work. The cube root of the density of a substance varies as the square root of attractive force between the molecules. When heat goes into a liquid to vaporize it, the heat must do work against the forces of attraction of the molecules The amount of work that has to be done would be expected to vary directly as the magnitude of the forces of attraction between molecules.

*To calculate the work required to compress 1629 cc of gas at 1 atmosphe e to 1 cc of gas at 1629 atmosphere.*

Consider first a cylinder of 1 sq. cm. cross section and 1629 cm long . The cylinder placed vertically, sealed at lower end and a movable piston at upper end,

Now if a weight be placed on the piston, the piston will sink, compressing the gas. The work done to produce this compression will be product of weight applied and distance through which weight has moved. If, now, a further weight is added, further compression and further work is done.

Consider, now, the reverse of this, namely, the whole of the weight applied, and successive removals of the weight. That is, a number of weights varying in size from 1629 to 1 atmosphere through a distance up to 1629 cm.

Consider a liquid at its boiling point.

Let P atmospheres = pressure to which an equal volume of gas would be subjected

Let S atmospheres = its pressure as gas.

Let 1 volume of liquid be taken,

Then this will form $\frac{P}{S}$ volumes of gas.

Then work required to convert 1 volume at P to $\frac{P}{S}$ volumes at S = sum of the products of the pressures at the various volumes from 1 to $\frac{P}{S}$ and the increase in volumes at the various volumes.

Original volume = 1.

Original pressure = P.

Let pressure be first decreased by $x$, that is, made $P - x$.

$$\text{The new volume} = \frac{P}{P-x}$$

$$\text{Let pressure next be made } \frac{(P-x)^2}{P}$$

$$\text{Then new volume} = \frac{P^2}{(P-x)^2}$$

$$\text{Let pressure next be made } \frac{(P-x)^3}{P^2} \text{ \&c.}$$

Work = increase in volume × pressure at volume, that is:—

$$\text{Work} = \left(\frac{P}{P-x} - 1\right)(P-x) + \left(\frac{P^2}{(P-x)^2} - \frac{P}{(P-x)}\right)\frac{(P-x)^2}{P} + \text{\&c.}$$

$$= \left(\frac{P-P+x}{P-x}\right)(P-x) + \left(\frac{P^2 - P(P-x)}{(P-x)^2}\right)\frac{(P-x)^2}{P} + \text{\&c.}$$

$$= x + x + x, \text{ \&c.}$$

$$= nx \text{ (where } n \text{ is the number of terms).}$$

But $\frac{P^n}{(P-x)^n}=\frac{P}{S}$

$\therefore n \log P - n \log (P-x) = \log P - \log S$

$$n=\frac{\log P - \log S}{\log P - \log (P-x)}$$

$$\therefore \text{work}=nx=\frac{x(\log P - \log S)}{\log P - \log (P-x)}$$

when $x$ is small this is convertible into the form
$\text{work}=nx=-P(\log_e P - \log_e S)$
or when S = 1 atmosphere
$\text{work}=-P \log_e P$ atmospheres (See note).

If original pressure was measured in atmospheres and 1 cc. of water was taken.

Work = 1629 $\log_e$ 1629 a mosphere centimetre grams converting into ergs.

Work = 1629 $\log_e$ 1629 × 76 cm × 13·5959 × 981

Atmospheric pressure; Density of mercury; Acceleration of gravity

= 1·221 × $10^{10}$ ergs.

Latent heat of 1 grm. of water = 536·6 × 4 188 × $10^7$ ergs.

Latent heat of 1 cc. of water =
536 6 × 4 188 × $10^7$ × 0 9586 ergs
= 2 155 × $10^{10}$ ergs.

Multiplying this last figure by 0 5746 $\sqrt[3]{\text{Density}}$ and treating other substances in a similar manner.

| Substance | P $\log_e$ P in Ergs. | Latent Heat | Density | Latent Heat × 0·5746 $\sqrt[3]{D}$. |
|---|---|---|---|---|
| Water | 1·221 × $10^{10}$ | 2·155 × $10^{10}$ | 0·9586 | 1·221 × $10^{10}$ |
| Ethyl Ether | 0 1401 × $10^{10}$ | 0·2695 × $10^{10}$ | 0·736 | 0 1397 × $10^{10}$ |
| Benzene | 0·1758 × $10^{10}$ | 0·3300 × $10^{10}$ | 0 82 | 0·1775 × $10^{10}$ |
| Oxygen | 0·1472 × $10^{10}$ | 0 2447 × $10^{10}$ | 1·124 | 0·1462 × $10^{10}$ |

This gives an agreement between the first and last columns equal to this accuracy of data used.

From this:—

P $\log_e$ P = Latent Heat × Density × $\sqrt[3]{\text{Density}}$ × con tant.

or P $\log_{10}$ P = Latent Heat × Density$^{\frac{4}{3}}$ × constant.

When Latent Heat is measured to 1 grm. of substance

$$\text{Latent Heat} = \frac{P \log_{10} P}{D^{\frac{1}{3}}} \times \text{constant}$$

$$= \frac{P \log_{10} P}{10\cdot31\ D^{\frac{1}{3}}}$$

*Relationship between Attractive Forces and Density.*

There are a number of assumptions made here which are contrary to accepted theory of matter.

(1) Molecules do not collide but pass sufficiently near to each other for the forces of attraction between them to be constantly altering the directions of movement of the molecules. The forces of attraction probably consist of ordinary gravitational force, together with surplus or unsaturated valency force.

(2) Molecules are without size.

(3) A liquid is merely a gas under the pressure produced by the attractive forces of its molecules.

(4) A solid is a liquid in which the attractive forces of the molecules are different in different directions.

(5) A crystalline solid is a solid in which the major attractive forces are all acting in one direction, and minor forces all acting in another, etc.

*Measurement of the forces of attraction of different substances.*

The kinetic energy of a molecule, whether it exists as a gas or liquid, is the same at any one temperature.

Consider the molecules as having kinetic energies which are constantly being reduced to nothing by the attractive forces, and afterwards having their kinetic energy restored. This is analogous to the action of the attractive forces of the sun on a comet, the kinetic energy of comet relatively to the sun being periodically reduced to nothing.

The mean kinetic energy of molecules will vary as the ratio of the weights of the molecules to the square of distance between them. That is, attractive forces between equal weights of molecules will vary as the square of distance between the equal weights.

Now the volume occupied by equal weights of a substance will vary as the density of the substances or the distance between equal weights will vary as cube root of density.

But forces of attraction vary as square of distance between the bodies.

That is the sum of all attractive forces of a volume of substance will vary as the two-third root of its density.

It must be noted that the attractive pressure of a substance (that is, the pressure at the surface of a substance) is not the same as the attractive force between the molecules. Neither is the one directly proportional to the other. The attractive pressure is P, which varies as $\frac{D}{M \times T}$

Where D = density as liquid
Where M = molecular weight
Where T = temperature of measurement

T becomes boiling point when measurements are made at the boiling points. P = the density of liquid compared with its density as vapour.

Attractive force varies as $(D^{\frac{1}{3}})^2$. That is as the square of distance between equal weights of substance.

Work required to overcome a force of attraction will vary as that force.

The work P $\log_e$ P is done on vaporisation by the kinetic energy of the molecules The work of overcoming the attraction of the molecules is done by the latent heat. They both have to be done to the same quantity of material through the same distance. In order to find the latent heat $D^{\frac{2}{3}}$ must be substituted for D in the expression $\frac{D}{M \times T}$

Now in the expression P $\log_e$ P, P represents the weight and $\log_e$ P the distance through which it is moved, so that $D^{\frac{2}{3}}$, instead of D, has only to be introduced into the P part of the expression P $\log_e$ P. Since P contains D the expression becomes

$$\frac{P}{D^{\frac{1}{3}}} \log_e P \times \text{constant.}$$

*Determination of constant* 0·5746.

The unit of density is 1 grm. of substance occupying 1 cubic centimetre. To divide space into cubic centimetres is not the most economical method hence the ratio of weight of substance to distance between weights is not as 1 grm. is to 1 cm. when density is 1. If, however, we put 1 grm. into the smallest space so that the centre of that space is always a centimetre from the centre of any neighbouring similar space then we have ratio of the weight of substance to the distance between the weights is as 1 grm. is to 1 cm. Now this space under these conditions must be greater than the volume occupied by a sphere of 1 cm. diameter since there would be loss of space between the spheres. It must also be less than the volume occupied by a hexagonal prism of 1 cm. between parallel sides and $\frac{\sqrt{2}}{\sqrt{3}}$ cm. height. Note that $\frac{\sqrt{2}}{\sqrt{3}}$ for height of hexagon is obtained when the hexagons in

layers of hexagonal prisms are not immediately above each other. The value of first $= \frac{\pi}{6}$ cubic cm. $= 0{\cdot}5236$ the value of second $\frac{1}{2}\sqrt{2} = 0{\cdot}707$ cubic centimetres. The required volume must lie between these two and probably be nearer the latter.

If the densities of substances are compared with a substance not of density 1 grm to 1 cc. but of 1 grm. to 0 6601 cc. then we can eliminate the constant 0·5746. Calling the density of a substance to this $\delta$ Latent Heat of 1 grm. $= \frac{P \log_e P}{\delta^{\frac{4}{3}}}$

Latent Heat of 1 grm. $= \frac{P \log_e P}{\delta^{\frac{4}{3}}}$ atmosphere centimetre grms.

## CORRESPONDENCE.

### GREAT NORTHERN CENTRAL HOSPITAL.

*To the Editor of the Chemical News.*

SIR,—The Lord Mayor has kindly allowed a meeting on behalf of the Great Northern Central Hospital, Holloway, to be arranged at the Mansion House, on the Eve of St. Luke's Day, October 17, at 3 p.m., in order to provide an opportunity of making known more widely the immense value to the Metropolis particularly, and the Nation generally, of the Institution's indispensable work; and in the hope that it may be a means of securing for the hospital the help which it needs so desperately at this critical time.

If the Hospital, which serves a large and densely populated area, with a million residents, is to continue without curtailing its work, it must have at least £22,000 before December 31, in addition to any income it can definitely expect to receive. It is to help in raising this sum that the Lord Mayor has so kindly allowed the meeting to be held.

Distinguished speakers will advocate the claims of the Hospital, and I do hope your readers will give their support, and if they cannot come to the to the meeting send a remittance, no matter how small, to me at the Hospital, so that an efficient hospital service in North London may continue.—I am, &c.,

NORTHAMPTON (*Chairman*).

## NOTES.

"OERTLING" BALANCES.—Sir Ernest Shackleton has taken an "Oertling" Balance with him on the *Quest*. An "Oertling" Balance was also taken by Admiral Sir George Nares on his expedition in 1873, and the same balance was used by the late Captain Scott in his expedition in 1901, and during the war it was used by the Engineering Department of the South Kensington Museum. It speaks well for the reliability of an instrument which can be of service 50 years after the date of its manufacture.

WE have received a copy of a new publication, *La France*, a journal that cannot fail to be of interest, especially to students and those wishing for a closer acquaintance with French and French every-day life. It will be published weekly, and give a general review of the daily, weekly, and monthly press. The paper can be obtained from any London newsagent, price 2d., or 2s. 6d. for a period of 17 weeks. The London address is Montague House, Russell Square, W.C.1.

DEVELOPMENT OF BRITISH INDIAN SUGAR INDUSTRY.—According to the Secretary of the Sugar Bureau at Pusa, states *Capital* (Calcutta), India has an annual consumption of 748,544 tons of foreign sugar, and is capable of finding over 15 crores of rupees yearly to meet her additional sugar purchases from abroad. As the price of sugar began to fall in September, 1920, a distinct tendency to import more became evident, despite the extra duty imposed As India's production of refined sugar is at present only 177,569 tons, it is obvious that there is ample scope for many times the number of factories now working in India. The prospect before the Indian sugar industry is very hopeful, as it can choose the most favourable parts of the country for supply for many years to come, and with the increased duty on foreign sugar, coupled with heavier freight and handling charges, it is considered that it would be well if capitalists devoted their time and attention more and more to developing the industry on a sound and scientific basis. There is ample scope and the rise in the cost of production through out the world, both of raw material and the finished product, has told heavily in India's favour.

"JOURNAL OF INDIAN INDUSTRIES AND LABOUR."—Part III. contains a fully illustrated description of the Government Acetone Factory by Mr. A. Appleyard, showing that a deal of good work has been and is being done at Nasik. A very interesting paper is given on "Indian Precious Stone" by Cyril Fox, Curator, Geological Survey of India. Crude alkali, which is plentiful in India, is being used with some success in the manufacture of a fair quality glass for bangles, &c., and a good account is given of the collection and refining of the salts of soda for this purpose by J. P. Srivastava and D. Sinha. There are many other interesting notes of more local interest.

A NEW PUBLICATION DEVOTED TO RADIOLOGY AND RADIOTHERAPY.—*Acta Radiologica*, published by the Societies for medical radiology in Denmark, Finland, Norway, and Sweden, contains articles pertaining to roentgenology, radium therapy, light therapy, and electrotherapy. These articles are published in English, French, or German, according to the decision of the author. Each volume comprises 500 pages, distributed in four occasional numbers. Subscriptions may be forwarded to the Editor. Subscriptions from America may also be sent to Mr. Paul B Hoeber, 67—69 East 59th Street, New York Cy. Subscription to Vol. I. \$6—32s. The work is fully illustrated with half-tone reproductions, and the first number contains the following articles: Editorial; "L'examen radiologique de l'ulcère du duodenum," by H. J. Panner; "The X-ray Diagnosis of Gallstones in the Common Duct," by M. Simon; "Ein Fall von Osteogenesis imperfecta mit verbreiteten Gefässverkalkungen," by Sven Johansson; "A Case of Arthropatia Psoriatica," by S. Ström; "Hemophilia and Hemophilic Arthropathy," by T. Klason; "A Case of Frac-

ture of the Cranium with Accumulation of Air in the Cranial Cavity," by N. Hansson; "A Plate-holder for Precise Roentgenography in Connection with Fluoroscopy," by Gosta Forssell; "Microscopic Examination of the Mucous Membrane of the Nose on Patients under Treatment for Lupus Vulgaris with Universal Arc-Light Baths," by K A. Heiberg and Ove Strandberg; "Plastic Means of Application and their Use in Radiumtherapy," by Lars Edling; "Die Intensitätsverteilung der primaren Gamma-strahlung in der Nähe medizinischer Radiumpraparate," by Rolf M. Sievert

## NEW COMPANIES.

The under-mentioned particulars of New Companies recently registered are taken from the Daily Register compiled by JORDAN & SONS, LIMITED, Company Registration Agents, Chancery Lane, W.C.2.

VICTOR H. IDDON, LIMITED —(177042)—Registered September 29th, 1921. 309, Holderness Road, Hull. To acquire and carry on the business of Vendor of Pharmaceutical requirements and Sundries. Nominal Capital. £1,500 in 1,500 Shares of £1 each. Directors· V. H. Iddon, 14, The Oval, Garden Village, Hull (Managing Director); E. H. Russell, 14, Village Road, Hull (Managing Director). Qualification of Directors. £50. Remuneration of Directors To be voted by Company

FRESSONS DRUG STORES, LIMITED.—(177033)—Registered September 29th, 1921. 177, The Broadway, Cricklewood, Middlesex To acquire and take over as a going concern and carry on the business of a Drug Store, now carried on by Charles Francis Fresson, at 177, The Broadway, Cricklewood. Nominal Capital· £1,500 in 1,500 Ordinary Shares of £1 each Directors· C F. Fresson, 177, The Broadway, Cricklewood, N.W.2. Herminia M. Fresson, 177, The Broadway, Cricklewood, N.W.2. Qualification of Directors: £10. Remuneration of Directors: To be voted by Company.

CARMOL, LIMITED —(176775)—Registered September 24th 1921 181, High Street, Blackheath, Birmingham. To carry on the business of Chemists and Druggists, etc. Nominal Capital £1,000 in 1,000 Shares of £1 each. Directors: A. S. Price, 181, High Street, Blackheath, Birmingham; R. T. Tiplady, 12, Bowkers Row, Bolton (Governing Directors). Qualification of Directors 25 Shares. Governing Directors: £50 each.

## New Patents.

THIS List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W C 2, from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously

*Latest Patent Applications.*

24203—Archer, M W—Method of producing white commercially pure ammonium chloride. September 12th

24415—Fairweather, H. G. C.—Recovery of nitrate from caliche. September 14th.

24658—Jones, H Sefton.—Manufacture of pure nickel. September 16th.

24670—Perkins, W. G—Treatment of copper ores. September 16th.

24456—Rodd, E. H—Manufacture of dye stuffs. September 14th.

24392—Plauson, H.—Process for treatment of rock phosphate, etc. September 14th

25298—Akt. Ges fur Anilin-Fabrikation—Manufacture of dyestuffs of the acridine series. September 23

24872—Brothers, W—Manufacture of sulphate of aluminium September 20th.

24831—Lancaster, H C.—Treatment of antimonial lead September 19th.

24799—National Aniline & Chemical Co., Ltd.—Seal for containers. September 19th.

25219—Plausons (Parent Co), Ltd—Manufacture of colloidal sulphur. September 23.

*Specifications published this Week.*

168627—Eustis, A H.—Method of and apparatus for the recovery of sulphur dioxide from furnace gases and other gases containing the same.

146939—Trent, W. E.—Method and apparatus for treating ores, chemicals, minerals and the like.

143872—Union Carbide Co.—Manufacture of calcium carbide.

150734—Pfannenschmidt, P L—Acid chambers, acid towers, acid mains and similar arrangements.

154888—Hartner, F.—Process for manufacturing a mortar forming material from anhydrite or the like.

161922—Riedel Akt. Ges., J. D.—Soluble mercury compounds.

145038—Johnson, J. Y.—Process for transforming ammonia into a salt for use as a fertilizer.

146289—Carpmael, W.—Manufacture of cynamide derivatives of alpha-halogenated acids.

146410—Clerc, A. and Nohoul, A—Manufacture of zinc sulphide

248242—Chemische Fabrik Rhenania and Vorkelius, Dr G. A—Manufacture of manures by breaking up phosphates with nitric acid.

*Abstract Published this Week.*

*Chromium Oxide Sodium Sulphide.*—Patent No. 166289.—A new process for obtaining chromium oxide and sodium sulphide has been Patented by Mr. C. J. Head, of Norfolk House, Laurence Pountney Hill, London The products are obtained by heating under reducing conditions a mixture of sodium chromate, sulphur and carbon in the proportions of $2Na_2$-$CrO_4$ 2S and 5C. The product is leached, the chromium oxide being washed, dried and calcined. The sodium sulphide solution may be evaporated to dryness. According to the Provisional Specification, the chromium oxide may be further purified by digesting with sodium carbonate solution, washing with hot water and drying.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

THE CHEMICAL NEWS.
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# BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

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## NOTES ON WATER POWER DEVELOPMENT.

ADDRESS DELIVERED BEFORE SECTION G (ENGINEERING)

BY PROFESSOR A. H. GIBSON, D.Sc., President of the Section.

(Concluded from p. 202).

WHERE accurate rainfall and evaporation records are available, it is possible to obtain what is often a sufficiently close approximation to the run off, but even rainfall records are not generally at hand where they are most required, and even in a district where such records are available, they are usually confined to easily accessible points, and are seldom extended to the higher levels of a catchment area where the rainfall is greatest. Even throughout the United Kingdom our knowledge of the rainfall at elevations exceeding 500ft. is not satisfactory, and little definite is known concerning that at elevations exceeding 1,000ft.

In this country evaporation may account for between 20 and 50 per cent of the annual rainfall, depending on the physical characteristics of the site, its exposure, mean temperature, and the type of surface covering. In some countries, evaporation may account for anything up to 100 per cent of the rainfall. As yet, however, few records are available as to the effect of the many variables involved. An investigation devoted to the question of evaporation from water surfaces, and from surfaces covered with bare soil and with various crops, under different conditions of wind, exposure, and mean temperature, would appear to be urgently needed. If this could be combined with an extension of Vermeulle's investigation into the relationship between rainfall, evaporation, and run-off on watersheds of a few characteristic types, it would do much towards enabling an accurate estimate of the water power possibilities of any given site to be predetermined

Even more useful results would follow the initiation of a systematic scheme of gauging applied to all streams affording potential power sites.

Among other questions which are ripe for investigation may be mentioned :—

(1) The combined operation of steam and water power plants to give maximum all-round efficiency.
(2) The relative advantages of high voltage D.C. and A.C. generation and transmission for short distances.
(3) The operation of automatic and semi-automatic generating stations.

*Tidal Power.*—The question of tidal power has received much attention during the last few years. In this country it has been considered by the Water Power Resources Committee of the Board of Trade, who have issued a special tidal power report dealing more particularly with a suggested scheme on the Severn. The outline of a specific scheme on the same estuary was published by the Ministry of Transport towards the end of 1920.

In France a special commission has been appointed by the Ministry of Public Works to consider the development of tidal power, and it has been decided to erect a 3,000 k.w. experimetnal plant on the coast of Brittany. With the view of encouraging research, the Government proposes to grant concessions, where required, for the laying down of additional installations.

The tidal rise and fall around our coasts represents an enormous amount of energy, as may be exemplified by the fact that the power obtainable from the suggested Severn installation alone, for a period of eight hours daily throughout the year, would be of the order of 450,000 horse-power.

Many suggestions for utilising the tides by the use of current motors, float-operated air compressors, and the like, have been made, but the only practicable means of utilising tidal energy on any large scale would appear to involve the provision of one or more dams, impounding the water in tidal basins, and the use of the impounded water to drive turbines.

The energy thus rendered available is, however, intermittent; the average working head is low, and varies daily within very wide limits, while the maximum daily output varies widely as between spring and neap tides.

If some electro-chemical or electro-physical process were available, capable of utilising an intermittent energy supply subject to variations of this kind, the value of tidal power would be greatly increased. At the moment, however, no such process is commercially available, and in order to utilise any isolated tidal scheme for normal industrial application it is necessary to provide means for converting the variable output into a continuous supply constant throughout the normal working period.

Various schemes have been suggested for obtaining a continuous output by the co-ordinated operation of two or more tidal basins separated from each other and from the sea by dams with appropriate sluice gates. This method, however, can only get over the difficulty of equalising the outputs of spring and neap tides if it can be arranged that the maximum rate of output is that governed by the working head at the lowest neap tide, in which case only a small fraction of the available energy is utilised.

When a single tidal basin is used it is necessary to provide some storage system to absorb a portion of the energy during the daily and fortnightly periods of maximum output, and for this purpose the most promising method at the moment appears to involve the use of an auxiliary high level reservoir into which water is pumped when excess energy is available, to be used to drive secondary turbines as required. It is, however, possible that better methods may be devised. Storage by the use of electrically heated boilers has been suggested, and the whole field of storage is one which would probably well repay investigation.

If a sufficiently extensive electrical network were available, linking up a number of large steam and inland water-power stations, a tidal power scheme might readily be connected into such a network without any storage being necessary, and this would appear to be a possibility which should not be overlooked in the case of our own country.

*Investigation necessary.*—A tidal power project on any large scale involves a number of special problems for the satisfactory solution of which our present data is inadequate.

Thus the effect of a barrage on the silting of a large estuary, and the exact effect on the level in the estuary and in the tidal basin at any given time can only be determined by experiment, either on a small installation, or preferably on a model of the large scheme.

Many of the hydraulic, mechanical, and electrical problems involved are comparatively new, and there is little practical experience to serve as a basis of their solution.

Among these may be mentioned:—

(1) The most advantageous cycle of operations as regards working periods, mean head, and variations of head.
(2) The methods of control and of sluice gate operation.
(3) Effect of changes of level due to wind or waves.
(4) The best form of turbine and setting and the most economical turbine capacity.
(5) The possibilities of undue corrosion of turbine parts in salt water.
(6) The best method of operation; constant or variable speed.
(7) Whether the generators shall be geared or direct driven.
(8) Whether generation shall be by direct or alternating current.

The questions of interference with navigation and with fisheries; of utilising the dam for rail or road transport across the estuary; and, above all, economic questions connected with the cost of production, and the disposal of the output of such an installation, also require the most careful consideration before a scheme of any magnitude can be embarked upon with assurance of success.

In view of the magnitude of the interests involved, and of the fact that rough preliminary estimates indicate that to-day current even for an ordinary industrial load could be supplied from such an installation at a price lower than from a steam generating station giving the same output with coal at its present price, it would appear desirable that these problems should receive adequate investigation at an early date.

*Facilities for Research in Hydraulic and Cognate Problems.*—In view of the considerations already outlined, and especially in view of the large part which British engineering will probably play in future water power developments, the provision on an adequate scale at some institution in this country of facilities for research on hydraulic and cognate problems connected with the development of water power is worthy of serious attention.

At present the subject is treated in the curriculum of the engineering schools of one or two of our universities, but in no case is the laboratory equipment really adequate for the purpose in question.

What is required is a research laboratory with facilities for experiments on the flow of water on a fairly large scale; for carrying out turbine tests on models of sufficient capacity to serve as a basis for design; and, if possible, working in conjunction with one or more of the hydro-electric stations already in existence, or to be installed in the country, at which certain large scale work might be carried out.

The provision of such a laboratory is at the moment under consideration in the United States, and in view of the rapidity with which the designs of hydraulic prime movers and their accessories are being improved at the moment, it would appear most desirable that the British designer, in order that the deservedly high status of his products should be maintained and enhanced, should at least have access to equal facilities, and should, if necessary, be able to submit any outstanding problems to investigation by a specially trained staff.

The extent to which our various engine laboratories have been able of recent years to assist in the development of the internal combustion engine, and to which our experimental tanks have assisted in the development of the shipbuilding industry, is well known to most of us, and the provision of similar facilities to assist in the development of our hydro-electric industry would probably have equally good results in this connection.

As a result of representations made by the Water Power Committee of the Board of Trade, I understand that it has now been decided to initiate a Chair of Hydro-Electric Engineering in some one university, and it is greatly to be hoped that funds may be available to enable the necessary laboratory to be designed and equipped on a scale commensurate with the importance of the work which it would be required to undertake.

## THE STUDY OF AGRICULTURAL ECONOMICS.*

ADDRESS DELIVERED BEFORE SECTION M (AGRICULTURE)

By C. S. ORWIN, M.A., President of the Section.

FOR the third year in succession the University of Oxford has been honoured by the selection of one of its resident members for the office of President of the Agricultural Section of the British Association, and on the occasion of the Edinburgh Meeting it may be of interest to recall that historically, at all events, the study of Agriculture and Rural Economy at Oxford takes second place to no university with the single exception of Edinburgh. I am not a scientist in the commonly accepted sense of the word, and nothing but my deep conviction of the need for wider recognition of the importance of the study of economics in connection with agricultural research work could have overcome my reluctance to assume an office in which I have been preceded by such a long line of distinguished men.

It is now about 25 years since research and educational work in agriculture began to be developed seriously in this country. Since that date, a very great deal of effort has been expended in investigating the forces by which plant and

*Read before the British Association, Edinburgh, 1921.

animal life are controlled, and to bring natural science to bear in every way upon the problems of food production. Work along these lines has been productive of most valuable results to the farmer; but at the same time the fact has been overlooked that, when all is said, farming is a business, and if it is to succeed as such, it must be carried on with a clear regard for the economic forces which control the industry. So, whilst desiring nothing but the fullest recognition of work in the fields of natural science applied to the investigation of farming problems, I must express without any qualification the view that the equal importance of the study of these economic forces has never been adequately recognised. Educational and research work in agriculture which takes no account of the dominant importance of economics must always be ill-balanced and incomplete, for farming business requires for its proper control a consideration of human relationships, of markets, of transport, and of many other matters which should come within the purview of the economist, as well as, or even more than, a consideration of questions regarding the control of plant and animal growth with which the scientist, in the limited sense of the name, is concerned. No one could wish to deny the need for the close and continual study of the soil and the means by which it can be made to produce more abundantly; no one could deny the need for research work in problems of animal and plant life. But the main concern of the farmer is to know not so much that which he can *grow* and how best to grow it as that which he can *sell* and how to sell it at a profit. Given the necessary capital and labour, conditions may be contrived under which any soil may be made to produce any crop; but the wisdom or otherwise of embarking upon any particular form of production can be determined only by a study of economic forces. In Bedfordshire, for example, considerable areas of very moderate land are met with given up to a most intensive form of agriculture; but land equally suitable for a similar form of farming may be met with in many other parts of the country which is not producing a tenth part of the value in food products nor employing a tenth part of the capital and labour, whilst at the same time the systems under which it is farmed are fully justified by the results. The reason of the difference, as doubtless everyone realises, is that the land in the former case is so situated that it has access, in the first place, to supplies of organic manures on an abundant scale and at a cheap price, and in the second place, to markets crying out for its produce, whilst one or both of these facilities are denied to the other areas. In the Chilterns district of Oxfordshire, farming a generation ago was mainly directed to the production of corn and meat, and nothing that has arisen out of the work of the investigators along lines of natural science would have called for any radical changes in agricultural policy on these soils. But economic forces, inexorable in their effect, have brought about a revolution, and arable land previously under corn and sheep is now laid down to grass or occupied with fodder crops for the maintenance of the dairy herds which have replaced sheep throughout the area. Again, in the hill districts of England and Wales there occur combes and valleys admirably adapted by soil and climate to the production of potatoes, and the highlands of Devonshire and Somerset may be cited in illustration. In these places, however, in the majority of cases, even though good markets may exist—Somerset, for example, imports potatoes—the lack of transport facilities makes it impossible for the farmers to produce anything which does not go to market on four legs Coming last to the question of human relationships, we find that it is possible to organise much more intensive forms of agriculture than any of our own, which would be an enormous advantage to a consuming nation like Britain; examples of such are to be met with in varying degrees of intensity in many countries. The Chinese, one reads, have increased production per unit area to an almost incredible extent, and in a lesser degree a similar state of affairs exists in parts of France and in Belgium (so often held up to us in this country as a model of productive capacity which we should strive to emulate). But in all these places the results are only achieved by a prodigal use of labour. The nation gains, no doubt, in the volume of produce available for its consumption, but the individual producer, deprived under this system of the opportunity to apply his manual effort in conjunction with an adequate amount of capital and land, is sacrificed to the consumer's advantage, and is driven to spend himself, year in and year out, for a reward for his toil which the British worker, with so many alternative openings in more profitable directions available for him under our industrial system, would never for one moment submit to. From what I have read, I imagine that the fact which drove so many Scottish crofters across the seas was much less the selfishness of deer-stalking landlords than the opportunity for exchanging a few acres of rocks and heather in the Highlands for 160 acres of the virgin soil of Canada. People only submit to poor conditions of life when they have no alternative, and one of the most important studies awaiting the investigator of agricultural economics is that of the lines on which to develop the industry so as to give the worker the biggest reward for his toil.

These few illustrations may serve to indicate the over-riding importance of the economic factor in forming just as in any other business. It is a common experience in industry that many scientific and technical processes are possible which are not profitable, and it is in the light of the profit that they leave that all of them must be judged.

Economic conditions are subject to continual change, and the variations may be both sudden and extreme. This makes it the more needful to be continually recording experience and to examine it for the facts that emerge from which to obtain guidance for future policy. Much information is required both for national and individual guidance. Of late years, for example, there has been much advocacy of more intensive cultivation of the soil; it is said that by closer settlement and more intensive methods the production from the land could be much increased. On the other hand, there are those who advocate a development of extensive farming as being the only means by which to attract capital to the land and to pay the highest wage to the worker. Both sides to this controversy can and do produce evidence in support of their views, and some

TABLE I.—*Production per Unit of Land and per Unit of Labour from Holdings of Various Sizes.*

| | Group | No. of Farms in each Group | Average size of Farms | Average Arable Land per cent. | Altitude | Average Rent per acre | Average Men per 100 acres | Sales per acre | Sales per man. |
|---|---|---|---|---|---|---|---|---|---|
| | Acres. | | | | Feet | s. d. | | £ s d | £ s. d. |
| I. | 0-50 | 5 | 39 | 17 | 341-369 | 32 10 | 7·1 | 11 19 11 | 168 19 0 |
| II. | 50-100 | 10 | 78 | 22 | 319-384 | 33 0 | 6·4 | 9 19 2 | 156 2 0 |
| III. | 100-150 | 14 | 138 | 21 | 370-453 | 27 2 | 4·2 | 7 19 1 | 189 0 0 |
| IV. | 100-250 | 11 | 201 | 11·7 | 330-411 | 28 4 | 3·3 | 7 5 8 | 222 12 1 |
| V. | over 250 | 12 | 356 | 18·0 | 286-435 | 26 5 | 2·6 | 8 4 4 | 316 19 0 |

TABLE II.—*Producer's, Wholesaler's, and Retailer's Prices for Market-Garden Produce, January,* 1921.

| Article | Cabbages, medium grade, per dozen | Cabbages, bottom grade, per dozen | Cauliflowers, top grade, per dozen | Sprouts, top grade, per 28lbs. | Turnips, medium gde. per cwt. |
|---|---|---|---|---|---|
| | s. d. | s. d. | s. d | s d. | s. d. |
| Producer | 0 3 | 0 2½ | 3 0 | 3 6 | 3 0 |
| Wholesaler | 1 0 | 0 9 | 5 0 | — | 5 6 |
| Retailers— | | | | | |
| (*a*) Stalls and Barrows | 2 6 | 2 0 | 6 0 | — | 14 0 |
| (*b*) Suburban shops | 3 0 | 2 6 | 8 0 | — | 14 0 |
| (*c*) Stores and high-class shops | 4 0 | 3 0 | 10 0 | 14 0 | 18 8 |

figures derived from a survey made by my colleague, Mr. J. Pryse Howell, will serve to illustrate both. The total area surveyed was 9,390 acres, divided into 52 farms of various sizes, and the region was selected by reason of the uniformity of the general conditions. All available data for each holding were collected, and after grouping the farms according to acreage, the figures were thrown together and averaged for each group, with results as shown in Table I.

It will be noted that the conditions under which the farming is carried on in the various groups show no material differences as between one group and another, except in the matter of area. There is a tendency for rent to fall as the size of the holdings increases, but it is not pronounced, and in one case (Group IV.) the percentage of grass-land to arable land is considerably higher than in the rest; but, considering the variations which must be expected in the conditions prevailing over any area of 15 square miles in extent, it may be claimed that in respect of altitude, quality of land, and proportion of arable to grass the holdings in these five groups are fairly comparable. Taking the results as they stand, the fact emerges that employment and production vary inversely with the size of the holding, but that the production per man employed varies directly with the size of the holding. Thus, on the one hand, the advocates of closer settlement and the intensive methods which must necessarily follow if men are to live by the cultivation of small areas of land would seem to be justified in that the results shown by the survey indicate the highest amount of employment and the greatest product-value in the smaller groups. On the other hand, the advocates of more extensive methods of farming can point to their justification in that it is clear that the efficiency of management is greatest in the larger groups if the standard of measurement be that of product-value per man employed.

However, it is clear that either party is drawing conclusions from incomplete data. The efficiency of any farming system can only be judged by an examination of the extent to which all the factors of production are utilised and balanced under it. Each of the assumptions made from the figures above ignores entirely the factor of capital. Land, labour, and capital are all required for production, and the *optimum* system of farm management is that which utilises all three together so as to secure the maximum result from each. If information were available as to the capital utilised in each of the five groups in the survey it might be found that in the smaller groups labour was being wastefully employed, and that an equal number of men working on a larger area of land with more capital, in the form of machinery equipment, would produce an equal product-value per unit of land with a higher rate of output per man employed. Equally it might be found that in the larger groups the use of more labour, or a reduction in the area of land, might produce the same product-value per man with a higher rate of output per unit of land. Obviously there can be no absolute answer to the question of what constitutes the most economical unit of land for farm production. The quality of land in certain cases, and market, transport, and climatic conditions in many more, make it impossible to determine even within wide limits the size of the holding on which the principal factors of production can be employed with maximum effect. Within similar areas, however, and in limited districts, much work can and should be done by agricultural economists to collect evidence on this point for the information of all concerned with the administration of land.

Another matter of the utmost importance to the former and to the public alike, and one which is crying out for investigation on a large scale, is the distribution and marketing of farm produce. Attention has been drawn at many times to the discrepancy between the price realised by the producer and the price paid by the consumer for the same article. In connection with market-garden produce, for example, the Departmental Committee on the Settlement or Employment on the Land of Discharged Sailors and Soldiers stated in their Report (Cd. 8182, 1916) that "the disparity between the retail prices paid for market-garden produce in the big towns and the small portion

of those prices received by the growers is utterly indefensible. It demonstrates a degree of economic waste which would ruin any other industry" No evidence was published by the Committee as to the facts upon which this conclusion was based, but a recent inquiry made by the Ministry of Agriculture into the prices prevailing at various stages in the distribution of vegetables in London may be quoted in confirmation of it. Figures were collected to show the amount received by the producer, the wholesaler, and the retailers for various classes of everyday garden stuff, with results as shown in Table II.

One has only to glance at the prevailing methods of distribution to realise their wastefulness. The street in which I live contains ten houses, and each day four milk-carts, three bakers' carts, three grocers' carts, and two butchers' carts deliver food to them. Twelve men, horses, and carts, not to mention a host of errand-boys on foot and on cycles, to deliver food to ten families! While we are content with such a loose organisation of distribution as this represents, we must not wonder if prices received by producers seem disproportionate to those paid by consumers, particularly when the produce partakes of the nature of market-garden stuff, bulky, perishable, and of low value. But apart from the question of methods of distribution, and the advantages to producer and consumer alike which would accrue from some co-operative organisation directed towards the elimination of unnecessary retailers who do no real service to either of them, an investigation of transport and marketing costs would show to what extent they are being exploited by the distributor. The farmer suffers equally with the market-gardener. At the present time I am getting 1s. 9d. per gallon for milk sold to a middleman from my farm, and for this milk my wife is charged 3s. per gallon I am selling lamb at 1s. 4d. per pound for which she is charged 2s. 6d. per lb., and if the drought had not upset the crop I should be selling potatoes at an equal disparity as between wholesale and retail prices. Can anyone say whether these figures do or do not represent a fair division of total cost as between producer, retailer, and consumer? It may be asserted with confidence that no one can speak with authority upon the subject. The only figures which we have been able to collect at Oxford on the cost of distribution relate to milk, and the most recent that we have are those for the year 1918. In that year in a Midland manufacturing town we found that the distribution costs of a large producer-retailer were as follows:—

| | £ | s. | d. |
|---|---|---|---|
| Labour: Manual and clerical ... | 1,242 | 10 | 2½ |
| Horse ... ... ... ... ... | 497 | 0 | 9½ |
| Rent ... ... .. ... ... ... ... | 75 | 0 | 0 |
| Sundry purchases, depreciation, general expenses, &c. . . ... ... | 430 | 2 | 1 |
| Total cost | £2,244 | 13 | 1 |

| | |
|---|---|
| Number of gallons of milk distributed | 112,833 |
| Cost of distribution per gallon ... | 4·77d. |

Doubtless the conditions have changed since that year, nor is it possible to generalise from a single example; but, nevertheless, the figure for the gallon-cost seems to indicate that both farmer and consumer are suffering in the interests of the distributor, though it is impossible to say without further investigation whether the profit secured by retailers generally is excessive, or whether the difference between distribution cost and the margin out of which it is paid is necessary owing to an excessive number of distributors.

As to the other points named, meat and potatoes, no evidence exists at all, and the position with regard to them and also to milk is only indicated to emphasise the need for a full investigation of the economics of distribution.

At the present time labour problems afford a useful example of the need for further investigation of the economic problems of agriculture. The agricultural industry has been fortunate in that it has escaped the serious labour troubles which have shaken many other industries so badly during the past few years. This has been due in part, no doubt, to the closer personal relations which exist between employer and employed in agriculture than in other enterprises, and in part to the intervention of that often unfairly criticised body, the Agricultural Wages Board, but agricultural employers have also to thank the fact that agricultural labour is difficult to organise. Much controversy in the past would have been avoided, and the possibility of future difficulties could be faced with more confidence, if all the facts relating to labour had been and were being studied over the country generally. The labourer is often blamed for results which are due to the inefficiency of the farmer as a manager. When wages were low it may have been that the labourer was the cheapest machine, but in proportion as his remuneration approaches more nearly to the standard of reward in competing industries, so will the necessity for making his work more productive be intensified. The value of the output from the farm per man employed is not the only measure by which to gauge the efficiency of the management, but is certainly one of primary importance. A man with a spade can dig an acre of land in about two weeks at a cost to-day of about £4 10s.; a horseman and a pair of horses can plough an acre in about a day-and-a-half at a cost of £1 15s.; a farm mechanic on a tractor can break up an acre in about a quarter of a day, and although in the absence of sufficient data the comparison cannot yet be completed by reference to the cost of motor ploughing, it is fairly safe to suggest that when all the factors are considered—speed, less dependence upon atmospheric and soil conditions, as well as actual cost—there will be a still further advantage to be derived by investing the manual worker with the control of mechanical power. Thus it may be that high labour costs to-day are due in many cases less to the inefficiency of labour and more to the inefficiency of management. In a recent issue of *The Times* an agricultural writer expressed the view that if the means existed for determining the proportion of the net returns of agriculture accruing to-day to labour, it would be found that labour was taking an excessive toll of farming results. This view is probably very generally held, and it affords a good example of the misconceptions which may and do arise in people's minds in the absence of exact information upon which to base their assertions. This happens to be one of the questions which have been the sub

ject of investigation at Oxford, though only on the small scale that the means at the disposal of the University has admitted. An investigation was made before the War of the Distribution of the Net Returns of Agriculture as between landlord, farmer, and labour. The net returns are calculated from the net output, and the net output was ascertained by the method followed in the Final Report on the First Census of Production of the United Kingdom, 1907 (Cd. 6320). Under this method the cost of materials at the works is deducted from the value of the output at the works, and the difference constitutes for any industry the fund from which wages, salaries, rent, royalties, rates, taxes, depreciation, advertisement, and sales expenses, and all other similar charges have to be defrayed, as well as profits. The same basis of calculation was adopted in the Report of the Board of Agriculture and Fisheries on the Agricultural Output of Great Britain (Cd. 6277) made in connection with the Census of Production Act, 1906. In applying this measure of net output to the agricultural industry, the method is to value the farmer's capital at the beginning of the year and to add to this figure all live and dead stock bought during the year, foods, manures, tradesmen's bills, on-cost and establishment charges, &c., and to deduct the total from the sales during the year added to the valuation of the farmer's capital at the end of the year. Only in the case of the workers is their share of this net output available as net income. The landlord has to incur a considerable expenditure upon the farm in the way of repairs and maintenance, and this must come out of his share of the net output. From an enquiry conducted by the Land Agents' Society in the year 1909, it appeared that about 30 per cent. of the rent received by the landlord is expended by him in repairs, insurance, management, and similar payments necessary to maintain the property in a condition to produce the rent. The farmer, too, may have certain expenses to meet not covered by those deducted in arriving at the net output, and his share of this figure has also to cover some rate of interest on his working capital, besides the reward due to him for the exercise of his managerial functions. Thus, in considering the distribution of the profits of agriculture between the three interests concerned, it is necessary to distinguish between net output as defined in the Census of Production and what may be termed the net returns. The net returns are ascertained by deducting from the net ouput any additional expenses of the business not already allowed for; a sum representing about 7 per cent interest on the farmer's capital (this figure being based in current rates for money), and one-third of the amount of the rent.

This method for calculating net returns was applied in 1913 to six farms scattered all over the country, and differing from each other in almost every way as to systems of management, soil, locality, and so forth, and it was found that the proportions accruing to each of the three interests varied hardly at all, and that it would be safe to say that 20 per cent of the total was going to the landlord, 40 per cent to the farmer, and 40 per cent to labour. Owing to the disorganisation of the work arising out of the war, it was not possible to carry on the investigation on each of these six farms, but it was continued in connection with one of them down to the year 1920. This farm may fairly be described as typical of "average to rather indifferent" conditions. It was a tenant-farm, about 1000 acres in extent, commanding a rent of less than £1 per acre, about three-quarters arable, situated on light to medium land, seven miles from a station, and farmed mainly for production of corn and meat. Taking the above proportions, namely, 40 per cent each to farmer and labour and 20 per cent to landlord as the pre-war rate of distribution, and calling each of these shares 100, the proportion of distribution between the three interests varied during the following six years as shown in Table III.

TABLE III.—*Distribution of the Net Returns from Farming between Landlord, Farmer, and Labour during the years* 1913-14—1919-20.

| Year | Landlord | Farmer | Labour |
|---|---|---|---|
| 1913-14 (Standard) ... ... | 100 | 100 | 100 |
| 1914-15 ... .. ... .. | 97 | 104 | 99 |
| 1915-16 ... ... ... .. | 94 | 108 | 98 |
| 1916-17 ... ... ... .. | 91 | 115 | 94 |
| 1917-18 ... ... ... .. | 90 | 111 | 99 |
| 1918-19 ... . ... ... | 87 | 115 | 98 |
| 1919-20 .. ... ... ... | 89 | 109 | 102 |

The figures are interesting in several ways. In the first place they seem to disprove the suggestion referred to above, that labour has been taking an undue share of the net returns from farming, for an examination of the figures in the "Labour" column shows that until the institution of the Agricultural Wages Board in 1917, the tendency was in the direction of a slight but steady reduction in the proportion coming to the workers; the effect of the Wages Board Orders was to steady this tendency and, ultimately, to bring labour back approximately to the position it occupied in 1913-14. If the figures could have been continued for another year, it is likely that they would show a material increase in the workers' share, but, even so, it would be found that this increase had been achieved without reducing the farmer's share below his pre-war proportion. In the second place, the figures confirm the experience of landowners in that the landlord has received no part of the increased prosperity of farming, whilst, as everyone knows, his expenses of maintenance have enormously increased. Briefly, the situation is that, thanks to the Agricultural Wages Board (and its appointed members may take heart from the fact), the workers have been maintained in the same position as regards their share in the net returns as that in which they were before the war, whilst the farmer has received his share in the increase realised during the past few years, together with that which would have gone to the landlord had the pre-war scale of distribution been maintained. Rents and wages under normal conditions are slow to adjust themselves to changes in farming fortune, and, except in a time of violent economic upheaval, it is right that this should be so, for if the landlord may be regarded as a debenture holder, and labour as a preference shareholder, then the farmer, as the ordinary or deferred shareholder, has to bear the brunt, and if he must take the kicks, so also is he entitled to the half-pence.

Turning now from problems in which either the nation generally or whole classes of the industry are concerned, it may be stated that there are

many economic problems arising on the farm itself in the solution of which the individual farmer should be able to derive help from the economist. Some of these problems are so simple that their solution should be obvious, but the fact remains that waste in its most easily eliminated forms is constantly to be met with on the farm. The need for the study of the economic use of manual labour has already been referred to in another connection, but, granted that the balance between the employment of land, capital, and labour on any farm has been established, cases are continually met with where labour is being mismanaged. It is a not uncommon practice at threshing-time to take the horsemen from their work to assist at threshing, and as this operation can only be performed in dry weather, it may be assumed that the horses might usually be employed on threshing days. With manual labour costing about 7s. 6d. a day, and horses about 5s. a day, the advantage of hiring casual labour for threshing, even at high rates of pay, will be obvious when it is remembered that the horseman whose horses are standing idle represents a daily cost for the manual work performed by him of some 18s. On a Midland Counties farm, where the maximum possible horse-hours in a certain week in November last were 238, the time actually worked by horses was found to be 87, owing to threshing operations, and the wastefulness of the labour-management in such a case is obvious Again, employers in certain cases object to paying Saturday overtime to men willing to work, because overtime payments are at a higher rate than those for ordinary time, but they overlook entirely the fact that the Agricultural Wages Board provides no overtime payments to the horses, and and thus the heapest horse-labour on the farm is that performed on Saturday afternoon at overtime rates of pay to the horsemen.

Everyone realises, of course, the importance of keeping horses busy, but not everyone thinks how heavily the cost of manual labour is increased by idle horses. The maximum number of working days in a year is 312, a total obviously impossible of attainment in practice. Such records as are available show that the days actually worked by horses on the farm will not usually exceed four-fifths of the maximum. More time may be lost in summer than in winter, a fact not generally realised, and the period of maximum unemployment falls between haymaking and harvest. The busy seasons are, of course, the autumn and the spring, when the preparation of the ground for winter and spring corn is going actively forward. In the year 1918, figures were collected to show the percentage of days worked compared with "possible days" in each month on four farms distributed pretty evenly over England, and the results, thrown together, are as follows:—

TABLE IV.—*Percentage of Days Worked to Possible Horse-Days on Four Farms in* 1918.

| | Per cent | | Per cent |
|---|---|---|---|
| January | 67 | July | 38 |
| February | 82 | August | 65 |
| March | 77 | September | 78 |
| April | 74 | October | 80 |
| May | 70 | November | 67 |
| June | 56 | December | 64 |

Although the figures represent an average of four farms, it is noteworthy that the results on the individual holdings varied one from another in degree only, and that the months of maximum and minimum employment were the same in every case. The loss of time is far more serious than many people realise. The maximum possible horse-days in the year are 312, and the cost per day of the horses on the above four farms on this basis was 2s. 7d., whereas, owing to the time lost, the cost on the basis of days worked was 3s. 7d. Whilst some difference is inevitable, so great a discrepancy as these figures reveal can be avoided by skilful management, and one of the tests of the farmer's efficiency is provided by an examination of the distribution of horse-labour throughout the year on his farm. His cropping and other work should be so contrived as to provide for the uniform utilisation of horse-labour month by month. Under skilful management the differences in the number of days worked by horses from year to year are extraordinarily slight. On an East Midlands farm, employing 23 horses, the days worked per horse during the past six years have been as follows. Days worked per horse. 1913-14, 250·25; 1914-15, 247; 1915-16, 243; 1916-17, 236; 1917-18, 243; 1918-19, 244·5.

It may be noted, in passing, that figures such as those given for the seasonal employment of horse-labour emphasise the need for a study of the place of the agricultural tractor in farm management, for the busiest times of the year synchronise, more or less, with the seasons when the weather is more uncertain and suggest that the application of speedier mechanical power to field operations, in substitution for slower horse-power, would result in economic advantages in certain cases

In connection with the study of economics on the farm, the question of agricultural costings naturally suggests itself. Farmers, as a class, are not accountants and much less are they cost accountants, but this has not deterred many of them from taking part in discussions of farming costs which have been going on in the Press and in the Food Controller's offices for some time past, and the confusion of thought on the question of what cost of production really is which these discussions have revealed is evidence of the need for study and education in costing processes. Few things can be of greater service to the farmer than scientific book-keeping carried out and interpreted with proper understanding, but few things can deceive him more than costing wrongly conducted or misinterpreted. The need for accurate thinking is evidenced in nothing, perhaps, so much as in conneciton with the question of the valuation of the raw materials grown on the farm, the hay, straw, roots, pasturage, &c., produced for home consumption in the process of manufacturing milk and meat. There can be only one basis of value possible, namely, their cost to the farmer, but it is contended, almost universally, that their market price should be substituted for the sums that he has actually paid for them. As a matter of fact, the bulky feeding stuffs usually produced and consumed at home rarely have any market value at all. A market value is one that can be realised in the market. Thus, corn, meat, and certain other commodities have clearly market value because they are always saleable, but if all the farmers in the country decided to sell their mangolds they would find that the market for mangolds is non-existent, and that the prices

quoted in market reports represent a few deals to satisfy an infinitesimal demand. The same is true of straw, and, in a slightly less degree, of hay in normal times. Even if the difficulty of fixing the market prices of certain products, such as turnips, straw, or hay, be ignored, and if it be assumed that there be a free market in such things, a fuller consideration of what the farmer really does in feeding them to his stock will show how inapplicable such values are to his case. The market value of an article is the figure at which a willing buyer and a willing seller can agree to do business. The farmer who contends that he is justified in "selling" his roots or hay to his stock is selling them, in point of fact, to himself, and seeing that there is only one party to the transaction there can be no market and, consequently, no market price. In the majority of cases each of these things is grown because the farmer has need of them in the production of the article or articles of food towards which his management is directed. If he could buy them more cheaply than he can grow them he would surely do so, but to regard himself as a merchant instead of a manufacturer, and then to trade with one department of his farm against another is to involve himself in paper transactions which have no foundation in fact, and which may lead to disastrous conclusions. To take, for example, the cost of milk production. It is usual to argue that hay consumed by the cow should be charged at its market price. It may well be that in consequence of a temporary or of a local demand it will pay a farmer better to sell hay rather than to produce milk, and one of the main functions of book-keeping is to enable him to make a decision on such points as this. But he cannot expect to have it both ways; if he sells hay he cannot produce milk, and *vice versa.* Many farmers contract at summer prices for their winter supply of feeding stuffs, but a man who has bought linseed cake at a pound per ton less than the price current at the time when he is consuming it would hardly think of charging it to bullocks at any other price than that which he actually paid, and it is this figure, the actual cost to him, which must be the measure of the value of all raw materials, whether they be bought in the market, or whether, for the sake of convenience and economy, they be grown on the farm.

Lastly, I want to urge, and particularly before a gathering such as this, the importance of agricultural economics in agricultural education. The fact is realised, no doubt, by many teachers, but until a sufficient body of data bearing on the study of farm management can be made available to them, it is impossible for them to give to the teaching of practical agriculture that solid economic basis which is fundamental, and the teacher is driven to include in his instruction much to which the economic test has never been applied and to exclude more for which no basis for teaching exists at all. Given the requisite body of information, it would not only be possible but necessary to recast the whole foundations upon which the teaching of practical agriculture rests.

I am not one of the few who appear to derive satisfaction from making comparisons unfavourable to British agriculture with that of other countries, but when we look at the work which is being done in the United States, in Italy, Germany, Switzerland, and even in Russia, before the war, it is surprising to reflect that the agriculturists of the nation which produced Adam Smith, Ricardo, and John Stuart Mill should have been so slow to realise the need for a fuller organisation for the study of agricultural economics.

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## THE CHEMISTRY OF COLLOIDS.

By HUMPHREY D. MURRAY,
Exhibitioner of Christ Church, Oxford.

This branch of science dates from an experiment of Thos. Graham in the year 1862 upon the rates of diffusion of various substances through animal membranes. When he came to examine his results, Graham found that he could divide all the substances he had examined into two classes, according to their rates of diffusion. He gave the name of crystalloids to those substances with a high rate of diffusion, and colloids to those with a low rate, thereby drawing a sharp distinction between the two groups. As time went on, however, many substances were found, which, according to their treatment, appeared either as crystalloids or colloids; and as their number increased, Graham's sharp line of demarcation was relinquished, the names colloid and crystalloid being retained to denote general states of matter, rather than definite classes of substances.

Besides the difference in their rates of diffusion, solutions of colloids are distinguished from those of crystalloids by other properties which they exhibit to a greater or lesser degree, and which, when taken together, serve to distinguish the two types of solution. These properties are:—

(1) Appearance of Brownian movement under the ultramicroscope.
(2) Exhibition of the Tyndall effect;
(3) A small osmotic pressure;
(4) The phenomena of cataphoresis and endosmosis;
(5) The phenomena connected with electrolytic coagulation.

All these properties lead to the conclusion that the so-called colloidal solution is not a solution in the true sense of the word, since it must contain more than one phase. It seems very probable that the "dissolved" substance is present, not in the form of simple molecules, but as comparatively large aggregates of molecules, which are still small in comparison with ordinary dimensions. A colloidal solution, therefore, is not truly homogeneous, although such a condition is somewhat difficult to define, and it stands half-way between a true solution on the one hand and a coarse suspension on the other.

If a colloidal solution is viewed by directly transmitted light it usually appears perfectly clear. If, however, a beam of intense light be projected at right angles to the line of vision, the solution appears milky, the phenomenon being known as the Tyndall effect. When a similar arrangement is viewed through a microscope, it is found that the light is diffracted by the colloidal particles, and they appear as constantly moving points of light. This constant motion was first observed by the botanist Brown in the case of pollen grains suspended in water, and for some time its explanation was uncertain. It is now

apparent, however, that the motion is due to the continual irregular bombardment of the scarcely visible particles by the completely invisible molecules of the liquid in which the particles are suspended. Observation of this movement through the microscope, notably by Perrin, has resulted in considerably increasing our knowledge of the molecular properties of liquids.

The methods of producing colloidal solutions are very numerous, and may be said to vary with each substance. Four general methods are, however, recognised :—

(1) *Physical.*—This includes the addition of a definite peptising agent, that is some active body, which (probably by adsorption) breaks down the substance from the massive state into a colloidal solution. Such action is seen in the effect of alkalis in peptising various metal oxides. Peptisation may also be brought about by washing out the coagulating agent from a precipitate, but it will only be successful if it is possible to remove completely the precipitating agent, and if coagulation has not gone too far. Under this head also is included the preparation of colloidal solutions by the gradual replacement of a solvent by an inert liquid : for instance, by slowly pouring a solution of mastic in alcohol into water.

(2) *Chemical.*—An example is the formation of colloidal solutions of metallic gold by reduction of solutions of gold chloride with tannin or formaldehyde. Von Weimarn considers it possible, by suitably adapting the conditions, to produce any precipitate in states of aggregation ranging from a definitely colloidal form to a coarse crystalline mass, and he has shown this to be true in the case of barium sulphate.

(3) *Mechanical.*—When a solid is ground extremely fine and the product treated with water, part of it will form a colloidal solution which will be more stable if a suitable peptising agent is present. This has been done in the case of several metals.

(4) *Electrical.*—If an arc be struck between two metallic electrodes under water, portions of the metal are disintegrated, and a colloidal solution results. Bredig and Svedberg, using water and other liquids, have produced colloidal solutions of Fe, Cu, Hg, Al, and other metals.

All the methods enumerated above aim at producing a particle which is small enough to be kept in motion by the Brownian movement. If such a particle be produced, it will stay suspended in the medium in which it was formed, and not precipitate under the influence of gravity. For complete stability, however, it is necessary that two particles shall not coalesce when they come in contact, which would follow from the surface tension of the particles; and to bring this about it is necessary that the particles shall be furnished with some protective envelope. This may be effected by the adsorption of another substance upon the surface of the particle; a second way, of which it is easier to treat, is that the particles shall carry an electric charge, and thus repel one another. If, then, the particles in a colloidal solution are made sufficiently small and are prevented from coalescing, the solution will be stable. What this size may be is a question of experiment, but we can say roughly that suspensions, emulsions, and colloids have particles whose radii are of the order $10^{-4}$, $10^{-5}$, $10^{-6}$ cm. respectively. This result is arrived at by using the ultra-microscope, and by filtering through collodion filters of definite composition, which retain all particles above a limiting size.

It was at one time thought that the charge upon the particles was due to frictional contact between the particles and the medium in which they were dispersed. Such an idea has now been discarded, but it has not been replaced by anything very definite. The general opinion as to the cause of the charge is divided under three heads; that the charge is due to the ionisation of some foreign substance present in the colloid at the moment of formation; that the charge is due to the actual ionisation of the colloid itself; or that the charge is due to the preferential adsorption at the surface of the colloid of ions present in the dispersion medium. No reliable method has as yet been found for measuring the absolute charge upon the particles, but rough measurements have been made, which are not even very concordant, from the movement of particles when placed between two charged electrodes (cataphoresis). It is obvious that under such conditions, positively charged particles will move to the cathode and negatively charged particles to the anode. It is thus found that metallic hydroxides, *e.g.*, $Fe(OH)_3$, methyl violet, and other dyes are positively charged in water; while colloidal metals, sulphur, sulphides, silicic and stannic acids, eosin, indigo, resin, &c., are negatively charged. An observation of Hardy's in this connection is interesting; he found that in acid solution albumin is positively charged, being negatively charged in alkaline solution, and neutral in pure water. This would seem to support the theory that the charge is due to the adsorption of the hydrogen or hydroxyl ion. By measuring the actual velocity of the particles under a known potential difference, and making certain assumptions, it is possible to calculate the potential difference between the colloid and the medium, and hence the charge upon a particle. In this way Lewis, from some data by Burton, deduced a rough value of $8 \times 10^{-8}$ E.S.U. for a platinum particle.

The stability of the particle is due, as has been said, to a mechanical or electrical layer. If in the latter case, the charge upon the particle is removed, or reduced, we should expect coagulation to occur; and it appears very probable that such indeed is the case. On the addition of electrolytes to many colloidal solutions, precipitation takes place when the concentration of the electrolyte reaches a specific value. It seems quite possible that what takes place is a continued adsorption of oppositely charged ions (or something of that nature) until the effective protection due to the charge upon the colloid is removed, and coagulation occurs. It is found that the most actively precipitating ions are those carrying an opposite charge, whilst the higher the valency of the ion the greater is its precipitating power. This generalisation is known as the Hardy-Schulze Law. Whetham deduced on the basis of the theory of probabilities that the precipitating power of a series of ions of the same sign is proportional to a constant raised to a power representing the valency of the ion. Both these so-called laws are very rough generalisations, and are often found to break down. They represent

probably a single law of somewhat more complex nature defining the adsorption by a particle, of oppositely charged ions.

The chemistry of colloids is as yet still in its infancy, but it has wide-reaching applications—in trades such as tanning, dyeing, and brewing; in agriculture and sewage disposal; and in physiology and pathology Its knowledge is very largely empirical, and further advance calls for unremitting research.

## THE FOURTH DIMENSION AND RELATIVITY.

By F. H. LORING.

If any pre-eminent scientist had been asked, not many years ago, to write a chapter in science which could be regarded as *complete and*, so far as it dealt fundamentally with certain phenomena, *beyond criticism*, he might have chosen Newton's Laws of Motion for the title of his essay. To-day Newton's laws hold good in their practical application for a large group of phenomena, but the principle of relativity has opened up a new and extensive field of knowledge in connection with these laws, so that Newton's equations are being superseded by a more complete set of equations—due mainly to Einstein and to some extent to Minkowski and to H. A. Lorentz—which satisfy all the requirements of Newton and solve additional problems which were not known to Newton—and this is accomplished without a change in the fundamental structure of these new equations.

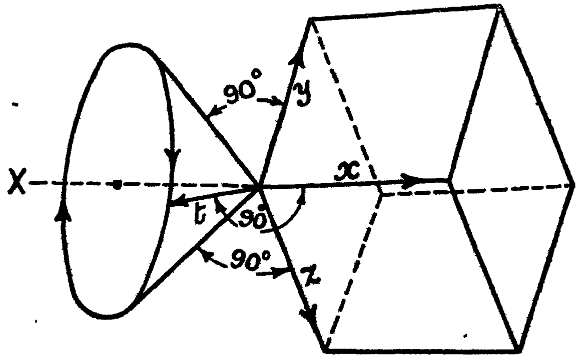
The mechanics thus created is very comprehensive, since it is applicable to light and to electricity, *i.e.*, to electro-magnetic-wave phenomena and to certain corpuscular radiations or motions, in particular to high-speed electrons. In general the presentment of phenomena is altered too.

No eminent scientist of to-day would regard Newton's laws as examples of crude and imperfect formulisations of fact. He would have the profoundest respect for Newton's great work, but he would have to admit that even the most complete, and at the same time the greatest mental achievement of man is not final for all time. The study of new phenomena in detail may any day add a new chapter to the most finished work even though it had been perfected to the highest degree by the contributions from leading experimentalists.

The advent of the new relativity doctrine has brought into prominence the idea of a *fourth dimension*, and it may not be out of place to discuss briefly the theory from this point of view. Those who take pleasure in studying such recondite problems as the *fourth dimension* may be interested in the following geometrical device used merely as an introductory illustration.

Construct a proper cone and a cube as shown and so place the former that it will give right angles between its surface and any one of the edges $x$, $y$, $z$, of the latter, as illustrated by the accompanying figure. The axis X of the cone will, if extended, pass through the diagonally opposite corner of the cube.

Now a line $t$ drawn on this cone will be at right angles to all the other lettered lines if it be imagined to revolve on the X axis at *infinite*




*Note*.—Angle of cone=70°·56; or 180°—70°·56 when the cone is formed round the three edges of a complementary cube This affords an interesting paradox, for how can an acute and an obtuse cone give the 90° angles specified? The reader may find pleasure in solving this problem that is not at first sight obvious.

*speed*, so as to lie in all places at once. Such a line, therefore, answers to the fourth dimension; but it becomes, in consequence of its rotation, a volume figure in effect and involves *time* in its realisation, even though infinite considerations come into the matter.

Devices of this kind may be helpful in a sense, but they must not be pressed too far; it is better to study the equations which contain the *fourth* dimension by implication.

Minkowski's conception of *time* and *space* is of interest here, for he says: "Henceforth space in itself and time in itself sink into mere shadows and only a kind of union of the two can be maintained as self-existent" His relativity equations give support to this view. Extension in the abstract would involve a dimension such as length in the abstract, but extension in the concrete, as when a body moves from place A to place B, involves time and space, time being consumed in the operation. Thus a time-extension becomes involved; and this affords perhaps a definition of reality which agrees with Minkowski's labelling as will be seen presently, or, as H. G. Wells has practically said—a thing has no real existence without being projected in time. An *instantaneous being* is a mere abstraction devoid of any semblance of reality; but given successive instants of time it becomes a *living thing* The terms "living" and "being" here refer to all matter. These are philosophical ideas but they have their counterpart or interpretation in the formulisation of physical phenomena along the lines laid down by Einstein, Minkowski, and H. A. Lorentz.

If now a point within the cube, as determined by three co-ordinates ($x_1$, $x_2$, $x_3$) be projected to a given time-place on the time-axis co-ordinate, or line considered as in rotation, a tube or cone would result which calls to mind Minkowski's *world-tube* idea, or *space-time filament*, as he also expressed it. The word "world" stands for physical phenomena: *i.e.*, point-time events, or real happenings. Minkowski's "world" can be described as a four-dimensional Euclidean space (continuum) which includes an imaginary time co-ordinate, and this has been given the mathematical symbolism $x_4 = \sqrt{-1}\cdot ct$ where $c$ is the velocity of light, and this special mathematical device gives symmetry to the equations. In this mani-

fold system, if one specifies movement, a standard of movement must be adopted, just as one of length is adopted, and as Minkowski's time-space idea involves movement, the velocity of light becomes the datum-line unit, as it were, in the system. This constant enters into the *fourth* dimension because it is common to all three axes which are in movement. The following, taken from Einstein's article in *Nature* (Feb. 17, 1921) is of interest in this connection.

| *Euclidean Geometry of Three Dimensions.* | *Special Theory of Relativity [Four Dimensions.]* |
|---|---|
| Corresponding to two neighbouring points in space there exists a numerical measure (distance $ds$*) which conforms to the equation $ds^2 = dx_1^2 + dx_2^2 + dx_3^2$ | Corresponding to two neighbouring points in space - time (point events) there exists a numerical measure (distance $ds$) which conforms to the equation $ds^2 = dx_1^2 + dx_2^2 + dx_3^2 + dx_4^2$. |
| It is independent of the system of co-ordinates chosen, and can be measured with the unit measuring-rod | It is independent of the inertial system chosen, and can be measured with the unit measuring-rod and a standard clock. $x_1$, $x_2$, $x_3$ are here rectangular co-ordinates, whilst $x_4 = \sqrt{-1} \cdot ct$ is the time multiplied by the imaginary unit and by the velocity of light. |
| The permissible transformations are of such a character that the expression $ds^2$ is invariant, *i.e.,* the linear orthogonal transformations are permissible. | The permissible transformations are of such a character that the expression for $ds^2$ is invariant, *i.e.,* those linear orthogonal substitutions are permissible which maintain the semblance of reality of $x_1$, $x_2$, $x_3$, $x_4$. These substitutions are the Lorentz transformations. |
| With respect to these transformations, the laws of Euclidean geometry are invariant. | With respect to these transformations the laws of physics are invariant. |

*(Quotation ends here).*

It should be noted that the term *invariant* means that there is no change in passing from one set of moving axes to another; or precisely, as a given alternating current phenomenon can be analyzed into working components, each one of which possesses the characteristic of *invariance* and observes a common law.

Relativity dynamics, or relativity equations involving a fourth-axis co-ordinate, regarded as representing time, enable problems hitherto unsolved to be solved when using the calculus and making each co-ordinate system a part and parcel as it were of each body in movement, so that in passing from one to the other the Lorentz transformation obtains.

Passing over considerable ground and turning to the culminating achievement of the theory in its more extended form (the *General* Theory of Relativity involving the Principle of Equivalence), the bending (or drawing-in—in the sense that converging railway lines would bring the trains closer together) of the course of light in passing close to the sun, owing to the concentration of the space-gravitational field (by analogy, the railway lines) round this massive body (due to the *mass-energy* of the sun as it might be termed), was clearly foreshadowed quantitatively by a development of the theory, and the phenomenon was verified by the photographs taken at the last total eclipse expeditions (see CHEMICAL NEWS, 1920, cxxi., 277).

*This is a distance between points exceedingly near together and it is called a *line-element*, which becomes a point event.—F.H.L.

## NOTE ON FIELDING'S FORMULA CONNECTING CRITICAL TEMPERATURES AND PRESSURES.

By J. NEWTON FRIEND,
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THERE is a certain fascination about numbers, and the application of mathematics to physical and chemical phenomena has revealed many laws and remarkable coincidences, which, in not a few cases, have proved of great value in elucidating intricate problems and in providing fresh avenues for research. Investigations of this type may be divided into two groups. To the former of these belongs that well-ordered and logical method of attack, which, based on certain assumptions, leads to the formation of laws, formulæ, &c., the correctness of which stands or falls, not by the method of calculation, but by the soundness or otherwise of the initial assumptions. A well-known illustration is Poiseuilles' famous formula for determining the viscosity of a liquid as derived by Laplace.

To the second class belong such coincidences and laws as are discovered by methods of trial, and not based upon any reasoned sequence. Kepler's laws of the planetary movements would appear to be an apt illustration Both methods have yielded very valuable results. In a series of papers appearing in recent issues of the CHEMICAL NEWS, various formulæ have been suggested by Fielding, in which numerical relations between certain physical data have been discovered. The method has clearly been that of trial and failure, and it is interesting to enquire whether the relationships are purely coincidences, or if they can be substantiated on theoretical grounds.

The formula given by Fielding (CHEMICAL NEWS, 1918, cxvii, 379) connecting critical temperatures and pressures, is

$$T_c = K\sqrt{p_c} + x$$

in which $T_c$ and $p_c$ are the international physico-chemical symbols for critical temperature and pressure, and $k$ and $x$ are constants.

This was arrived at purely by trial and error, and undoubtedly represents the fruit of an enormous number of calculations.

Now a consideration of van der Waals' equation

$$\left(P+\frac{a}{V^2}\right)\left(V-b\right)=RT$$

leads to the following well-known relationships between $p_c$, $T_c$, R and $a$ and $b$.

$$p_c=a/27b^2 \quad \text{(i)}$$

$$RT_c=8a/27b \quad \text{(ii)}$$

whence $27b^2=64a^2/R^2T_c^2 27$ ... ... ... (iii)

From (i) and (iii) it follows that

$$p_c=27R^2T_c^2/64a$$

$$\text{or } T_c=\frac{8}{R}\sqrt{\frac{a}{27}p_c}$$

Now if $\sqrt{a}/R$ remains fairly constant, as is quite within the bounds of possibility, at any rate for allied elements, such as the halogens, it is clear that the equation may be written

$$T_c=K\sqrt{p_c}$$

Where K is a constant and equals $8\sqrt{a}/R\sqrt{27}$. This expression is the essential feature of Fielding's equation. It is hardly to be anticipated that $\sqrt{a}/R$ shall be even approximately constant for *all* the elements, and Fielding finds that there are notable exceptions. The equation holds well for hydrogen and the halogens, but oxygen and nitrogen yield divergent values. There is thus seen to be a theoretical foundation for Fielding's empirical formula, and a theoretical explanation for its very obvious limitations.

## SPECIFIC HEAT OF VAPOURS

### Determination of Specific Heat of a Vapour at Constant Pressure $C_p$.

By J. C. THOMPSON.

The following method though not theoretically sound is fairly correct in its result.

Suppose 1 grm. of water at 4° C. be converted into 1 grm. of gas at 1 atmosphere pressure. This of course, is impossible as the Attractive Pressure exceeds 1 atmosphere at this density. Suppose this excess of attractive pressure to be small (or better to be compensated for in calculation at 5° C.), then the work to do this is

$$P_4 \log_e P_4 \times \frac{0{\cdot}5746}{D_4^{\frac{4}{3}}}$$

measured in atmosphere grms. D is equal to unity.

Suppose 1 grm. of water at 5° C. be converted into gas in a similar manner, then the work to do this will be

$$P_5 \log_e P_5 \times \frac{0{\cdot}5746}{D_5^{\frac{4}{3}}}$$

Now the difference between these two works converted into ergs will equal the specific heat of water in ergs from 4° to 5° less the specific heat of water vapour at constant pressure in ergs.

On calculating work at 4°, the figures $3910{\cdot}059 \times 0{\cdot}5746$ in atmosphere grm. centimetres and at 5° $3926\ 164 \times 0{\cdot}5746$ are obtained.

The accuracy of these calculations is not correct to seven figures, but as regards their difference, is probably correct to six figures. The difference between these two in ergs$=2{\cdot}160\times10^7=$Specific Heat of Water$-$Specific Heat of Steam$=4{\cdot}188\times10^7-2\ 028\times10^7$; or Specific Heat of Steam$=\frac{2{\cdot}028}{4{\cdot}188}=0\ 4843$ grm. calories; or if Specific Heat of Water from 4° to 5° is taken at 1·004 grm calories, Specific Heat of Steam=0·48 grm. calories. Experimental result at higher temperature=0 49.

*A Few Explanations.*

(1) *Molecules do not collide, but pass sufficiently near each other to have their directions altered by the attractive forces acting between the molecules.*

The forces gravitational alone between molecules, even though the molecules be small in weight and large in size, must be great at the small distances at which the molecules are apart. A very small acceleration at right angles to the initial velocity of a molecule would prevent their collision. Or a very small velocity at right angles to the forces of attraction between two molecules would prevent the collision of molecules. Suppose collision of molecules to take place, in the gaseous state at least, before a collision takes place the molecules must have passed very close to thousands of molecules before the collision actually takes place. There is no collision between stars, and only on the assumption of very large molecules and very small forces between them can collision take place in gases. Take the first—the assumption of very large molecules compared with their distances apart. This can only be true if molecules expand on passing from liquid to gaseous state. If molecules make this big expansion, it does not seem probable that they are perfectly elastic spheres. The second assumption—that the forces of attraction between molecules is small is highly improbable. Consider water gas at 100° C. and 1 atmosphere pressure; the slightest increase of density makes the gas quite independent of external pressure; that is, there ceases to be an external pressure. On the collision theory, the collisions must still go on and be counteracted by some other force. This force must be at 100° C. be less by an infinitesimal amount than the force required to produce 1 atmosphere pressure. Which is by no means a small force compared with the weight of substance.

(2) *Molecules have no size.*—This should be rather stated that the size of molecules does not in any way influence the volume occupied by a liquid.

(3) *A liquid is a gas under its own attractive pressure*—This is more or less accepted, together with considerable size to molecules. The pressure, of course, will vary with the size and other properties given to molecules. When a property, as Latent Heat, is related to a force that assumes no size to molecules, either the molecules have size which is also related to the Latent Heat, or they have no size. The latter assumption is far more probable. It would be as well to mention here that any change in the size of molecules is believed to be accompanied by optical and electrical phenomena, the kinetic energy of the parts of the molecule, and hence the size of the molecule bearing a similar relationship to the electrical potential, as the kinetic energy of the molecules, and hence the density of the substance does to the temperature.

*Compressibility.*—A liquid apart from the surface is incompressible until a pressure equal to the attractive pressure is applied.

*Meniscus.*—A meniscus will be formed when the attractive pressure exceeds the applied pressure.

*Solubility.*—Two liquids, not miscible, form a miniscus when in contact with each other. (Where ionization takes place another factor is involved).

At applied pressures exceeding the attractive pressure of the substance with highest attractive pressure, all substances are miscible. This should take place about seven miles beneath the sea-level —hence the earth's interior becomes homogeneous and doubles its density every seven miles. Also no mountain could exceed seven miles in height, unless constructed of some specially light material.

The attractive pressure of a vapour is equal and opposite to the vapour pressure at that pressure.

The surface of a liquid must be considered as being at pressures which vary from the applied pressure to the attractive pressure.

(4) A solid is a liquid in which the attractive forces of the molecules are different in different directions.

This follows directly from the theory of a liquid and explains the increase or decrease in density on solidification of a liquid.

This readily explains the hardness and elasticity of solids. It may be possible that a solid always consists of a number of minute crystals.

(5) A crystalline solid is so arranged that equal forces always act in the same direction.

The growth of a crystal from solution is explained on this hypothesis, as the molecules in separating from solution will attach themselves to the small crystal so that the greater forces act upon the greater forces.

A crystalline solid will have different attractive pressures in different directions, and hence different coefficient of expansion in different directions. A crystal, too, will have different densities in different directions. The double refraction of light in crystals points to different densities in different directions. Both the refraction of light and density depend on attractive pressure.

## NOTICES OF BOOKS.

*Coke-Oven and By-Product Works Chemistry.* By THOMAS BIDDULPH-SMITH, F.C.S. Pp. x.+196. London. C. Griffin & Co., Ltd, Exeter Street, Strand, W.C.2. Price 21s.

The author has written this book for the guidance of the coke-oven and by-products works chemist, for the various works on chemistry applied to gas manufacture, although extremely useful, do not by a long way meet his requirements.

The contents of the book comprise the methods of sampling and analysing the coal, coke, and gas, and later in the book the sampling and analysis of the products of distillation of coal tar, for example, benzol, the estimation of xylene in solvent naphtha, &c. The author also gives chapters dealing with the working of different plants, such as the tar distillation plant, the ammonium sulphate plant.

The book contains two appendices. Appendix I. gives a *resumé* of the properties of some of the constituents of coal tar, a translation by Percy Edwin Spielmann, Ph D., B.Sc., F.I.C., A R.C.Sc. In this Appendix, reference to German literature and patents have been retained, in order to serve as a guide to information which may not otherwise be very readily found.

Appendix II. gives a list of data useful to the chemist working in the laboratory. The chemist or works manager working in the above industry would find this book a great help to him.

*The Clayworkers' Handbook.* By ALFRED B. SEARLE. Third Edition. 1921. Pp viii+381. London: Charles Griffin & Co., Ltd, Exeter Street, Strand, W.C.2.

The whole field of clayworking is explored by the author in a very comprehensive manner. He first deals with the materials used in clayworking, namely, clay and its varieties, glazes, frits, colours, water, fuel, oils, and lubricants.

The second chapter deals with the preparation of the clay from the mining and quarying, through the intermediate stages of sorting, weathering, cleaning, grinding, mixing, and pugging.

The author in the third chapter devotes his attention to describing the machinery required for the operations enumerated above, giving methods of obviating troubles such as the formation of scale in boilers, also formulæ for the interpretation of results as, for instance, the transmission of power by belts, &c.

The chapters following this deal with different processes for the production of the finished article. Chapter XI. on "Defects" gives a list in alphabetical order of the different defects more commonly met with in clayworking, and methods for obviating same.

Chapter XIII. goes into the subject of testing and analysing the clay and clay products very thoroughly. The book ends with an Appendix of general information which will be found most useful to the clayworker.

The author is to be congratulated in collecting such a lot of valuable information and putting into such a concise and intelligible form.

*A Dictionary of Chemical Terms.* By JAMES F. COUCH. New York: D. van Nostrand Co. 1920. Price $2·50.

This book is designed to serve the convenience of those who have occasion to read chemical literature. New terms are continually being introduced into chemical science, and it is often difficult to arrive at a clear definition of their meanings. The treatment of the terms in the book is designed to lie between that of a standard English dictionary and that of an encyclopædia. The author, in his preface, while stating that every effort has been made to ensure accuracy, invites the fullest criticism, in order that errors may be eliminated in future editions.

The work is very well printed, and contains a fund of matter in a very small space that will be found of great value, both in schools and in the laboratory.

*Principles of Wool Combing.* By HOWARD PRIESTMAN. Second Edition, revised and enlarged. Pp. viii.+236. 1921. London: George Bell & Sons, Ltd. Price 12s. net.

The present new edition of this work has been thoroughly revised. Descriptions of machines that have become obsolete have been removed, and new types of machinery introduced in their place. The book is necessarily of a very technical character, but the wool industry is one of such supreme importance that an authoritative work on the principles that underlie wool combing will undoubtedly be found of great value. The book is illustrated by a great many diagrams connected with machinery used in the wool industry, and from the descriptions of operations it is evident that the author is thoroughly acquainted with the technique of the subject.

Many of the operations of wool dressing have been completely revolutionised of late years, and the author contrasts the practice in the good old days with that of the present time, which shows, even to the uninitiated, that the introduction of scientific methods is rapidly replacing the old rule of thumb practices of the past. The book is well indexed and contains nearly 100 illustrations.

*First Course in General Science.* By FREDERICK DELOS BARBER, A.M., MERTON LEONARD FULLER, N.D.I., M.A., JOHN LOSSEN PRICER, A.M., and HOWARD WILLIAM ADAMS, B S. 607 pp. Fully illustrated. New York: Henry Holt & Co. London: G. Bell & Sons, Ltd. Price 9s. net.

The aim of the authors has been to present a first course in general science for the use of the high schools. The scope of the book is very general, and technicalities are carefully avoided, so that the tone of the book approaches very closely to that of Pepper's "Playbook of Metals," which is familiar to a great many of us, written at a time when science was far less general than it is at present. The approach to each new topic is made from a historical point of view, with the object of developing an interest in the subject. The earlier chapters are more or less elementary, and as the ability of the pupil grows, the work becomes progressively technical A marked feature of the book is the immense number of original illustrations of a very varied character, but they certainly help greatly to make clear descriptions of apparatus and experiments that must of necessity be brief. We cannot help thinking, however, that the book would have been better for the omission of many of the plates. For instance, in a chapter dealing with dust and its dangers, a description is given of the vacuum cleaner, and half-a-page is taken up with a picture of a very beautiful young lady manipulating the vacuum cleaner while a gentleman is apparently having his breakfast at the same moment. There are a great many other illustrations of this type that are more suitable to a manufacturer's catalogue than to a book dealing with general science.

The line blocks of technical apparatus are very good, but the half-tone blocks are very inferior on account of the rough surface of the paper. Some of the portraits of men well known in science are very poor indeed.

There is a good Appendix at the back of the book devoted to weights and measures and the metric system, and a glossary of the terms used in the book which would be found of very great use.

*Introduction to Textile Chemistry.* By H. HARPER A.R.C.Sc., B Sc., A.I.C. Pp. x.+189. 1921. London: Macmillan & Co., Ltd. Price 3s. 6d.

Students thinking of taking up textile chemistry will find this small book a useful introduction to the subject. Descriptions are given of the various natural and artificial fibres used, together with the special tests and reactions for each, and definitions of the technical terms connected with their preparation or manufacture. Simple experiments are described which illustrate special points in the text. Supplementary chapters on oils and soaps, water-tests for textile fibres, and the chemicals used in textile manufacture contain a great deal of useful information The book is completed by a series of mathematical and other tables, and a glossary of chemical terms.

*Text-book of Qualitative Analysis of Inorganic Substances.* By S. A. KAY, D.Sc. Pp. viii.+80. 1921. London: Gurney & Jackson. Price 7s. 6d. net

The chief points of difference between this little book and others of a similar type are, firstly, that actual analytical procedure is described more minutely than is generally considered necessary in an introductory text-book, and secondly, that all experiments and reactions are carried out with very small quantities of materials. The author's reasons for these differences are that if the student can learn the experimental details from the book, the teacher will be able to discuss more freely with him the underlying principles upon which the procedure is based, and also that the use of small quantities of material tends towards greater accuracy in analysis as well as economy in reagents and apparatus. We are in full accord with the author's aim and wish the book every success.

## CHEMICAL NOTICES FROM FOREIGN SOURCES

*Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences.* Vol. clxxiii., No. 12.

"Action of Emulsine of Almonds on Lactose in Ethyl Alcohol Solution at 85°. By M. Marc Bridel.

No 13.

"The Corpuscular Spectra of the Elements." By MM. Maurice and Louis de Broglie.

## NOTES.

THE current number of the *Scientific American* publishes a paper by Mr. E. F. Cone, entitled, "The Divining Rod made Respectable"; an editorial note secures the *Scientific American* from any responsibility concerning the statements made, which is perhaps wise; a great deal is said about X-rays, radium radiations and the like, and then the inventor claims to have made a machine that can respond to any specific radiation said to proceed from all substances, "cartridges of the material sought for are placed in the device; the mechanism then synchronises the emanations . . . and locates the definite confines of the material in the earth," no matter how deeply they may be

buried, and as for oil fields and pockets of natural gas, it is said that a 100 per cent record was made in the location of new oil pockets or fields. It is hardly necessary to add that a company has been formed to exploit the invention.

BIRKBECK COLLEGE.—Mr. L. Bolton, winner of the £1,000 prize offered by *The Scientific American* for the best essay on "Einstein's Theory," will give two lectures on "Relativity" at Birkbeck College, Fetter Lane, E.C.4, on Mondays, October 24 and 31, at 5.30. Admission is free, without ticket.

UNIVERSITY OF BIRMINGHAM CELEBRATES ITS MAJORITY.—The University of Birmingham is just 21 years old. It is an outgrowth of the Mason Science College, founded in Edmund Street, Birmingham, by Sir Josiah Mason, the penmaker, and opened in 1880 Gradually its scope was enlarged, and it became known as the Mason University College, indicating a further advance in status, which prepared the way, under the fostering care of Mr. Joseph Chamberlain, M.P., for its expansion in 1900 under Royal Charter into a University, with its own Faculties and Degrees. The Arts and Medicine sides of the University remain in Central Birmingham, but the Applied Science and technical work is done at noble buildings at Edgbaston (three miles away), on a site of 45 acres. There are the great metallurgical and mechanical, electrical, and civil engineering blocks, as well as the departments of Chemistry and Physics, Mining, and Petroleum Technology. The unique event was celebrated by a Conversazione, which took place on Friday last at the Edgbaston University Buildings. The guests, who numbered 900, were received by Sir Gilbert Barling, Bart., the Vice-Chancellor, with whom was Mr. C. Grant Robertson, the Principal, and the Deans of various Faculties. The Lord Mayor (Alderman W. A. Cadbury), headed the Civic Representation The seven counties surrounding the City, which constitute the sphere of influence of this great Midland University, were all represented. In the various departments, experiments were performed by the Professors and their staffs to illustrate in a limited degree the scope of the University's activities, both the teaching and research. The close alliance of science and industry was noticeable everywhere.

NOTES FROM NORWAY.—Papers read before the Physical Society of Kristiana, September 23, 1921: "The Structure of North Light and the Nature of Cosmic Rays," by L. Vegard; "Variation in the Pressure of Gases caused by Electrostatic Forces," by O. E. Trivold. Norwegian Chemical Society, Kristiana, October 3, 1921: "The Occurrence of Scandium and its Compounds," by L. Schetelig.

TRADE DEPRESSION.—The Executive Committee of the Federation of British Industries have prepared a Memorandum which has been forwarded by their President, Sir Peter Rylands, to the Prime Minister. The report, which unfortunately is too lengthy to reproduce in the CHEMICAL NEWS, deals with the problem in a very masterly manner. It first briefly outlines the causes of the present depression, discusses the restoration of stability, and suggests possible measures for alleviating the difficulties of the next few years, and other factors, the final conclusion is put so clearly, and is of such vital importance that we reproduce it in full "We have got to realise that if we are to sell goods to an impoverished world we must sell them at a price which that world can afford to pay, and that if foreign labour costs are below ours in any trade, either through their workmen accepting lower rates of remuneration than ours, or giving higher efficiency for similar remuneration, no artificial measures will enable us to continue to give employment in that trade. The lowering of the cost of production involves of course two factors; the first is the improvement of management, organisation, and plant, and requires time, and above all, the expenditure of capital which war and present taxation and the diminution of the world's capital resources will render it extraordinarily difficult to supply. The second factor is either an increased efficiency of labour in proportion to its remuneration, or decreased remuneration without a decrease in efficiency. The choice before the country is to reach this result either by agreement which would be infinitely the quickest and most satisfactory to everyone concerned, or by sheer force of circumstances—continued unemployment, continued distress, and in the ultimate resort starvation for the workman and bankruptcy for the employer.

QUEENSLAND'S SALT LAKE.—The State of Queensland, as well as the American State of Utah, has its salt lake, and the following particulars of this natural feature of a country rich in mineral and agricultural resources, are of more than usual interest. According to Australian advices, some local operators, the Herrod Bros., of Bowie Station, brought in an interesting collection of specimens obtained on the shores of Lake Buchanan. Lake Buchanan is a salt lake situated on high country about 150 miles south-west of Pentland. The specimens are the head and bones of a bullock, which died on the shores of the lake. These bones carry deposits of salt, and the skull is encrusted in salt. As the water recedes, salt is left on the foreshores of the lake, and at present it is estimated that an expanse of twelve miles by four miles of this foreshore is exposed. This beach carries beautiful white salt of very fine grain, from 1ft. to 3ft. deep. 200 large bags of salt were obtained recently in this spot in two days. On the bones brought into town, lumps of pure salt, about 2in. or 3in. thick were encrusted, while the forehead of the skull carried 2in. of pure white salt. Given cheap carriage, there should be money in the natural salt deposits of Lake Buchanan. Wild fowl live in thousands on these waters, but the water is too salt for stock The lake is about 32 miles long by 8 at the widest part. It is a huge oval, and in a dry time it is possible to drive across it on the salt-crusted surface. In fact, the Herrods drove a buggy and pair across it quite recently, the crust of the salt being estimated at from 8in. to 1ft. deep. A horse is usually ridden on it to test the surface. After rain, this lake is a mass of game—swans, ducks of all sorts, geese, cranes, and pelicans in droves. Pelicans nest in the small islands in this lake, in fact, these islands are havens for incubation and eggs are everywhere. There are

many swamps of fresh water quite handy to Lake Buchanan, which are full of game. The method adopted by the Herrods when collecting salt is to scoop the salt in heaps in shallow water, and then shovel it into kerosene tins which have been freely perforated. The water drains off, and good clean salt remains. This is a cleaner and better way than shovelling it from the foreshore where the salt contains grass and twigs, and is not so clean. Tons and tons of this salt are on the foreshores of the lake. This lake is in a mountain depression, which forms the catchment for it. It is on no watershed.

## NEW COMPANIES.

The under-mentioned particulars of New Companies recently registered are taken from the Daily Register compiled by Jordan & Sons, Limited, Company Registration Agents, Chancery Lane, W.C.2.

Daniel Vahrman, Limited—(177125)—Registered October 5th, 1921 To carry on the business of chemists and druggists. Nominal Capital: £1,000 in 1,000 Ordinary Shares of £1 each. Directors: D. Vahrman, 76, Brick Lane, E 1. (Governing Director and Chairman), Mrs. P. Vahrman, 76, Brick Lane, E 1. Qualification of Directors £25. Remuneration of Directors. £500 Governing Director.

Anglo-Continental Metals, Limited.—(177066)—Registered October 1st, 1921 5, Bishopsgate, E.C. To carry on the business of Exportors and Importers of Ferrous and Non-Ferrous Metals and Metal Products Nominal Capital £10,000 in 8,000 Preference Shares of £1 each, and 40,000 Ordinary Shares of 1s each Directors W. M. Warman, 17, Hogarth Road, Earls Court, W., J W Maidment, 17, Hogarth Road, Earls Court, W. Remuneration of Directors To be voted by Company in General Meeting.

## New Patents.

This List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W C.2, from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

26042—Adelantodo, L—Manufacture of superphosphates and manure. October 1.

25562—American Cellulose and Chemical Manufacturing Co Ltd.—Treatment of cellulose derivatives. September 27

25586—Bloxam, A G.—Manufacture of ortho-oxy-azo dye-stuffs September 27.

25862—Freeth, F. A.—Production of ammonium chloride and sodium carbonate. September 30.

25937—Pauling, H—Method of transforming into sulphates metals and alloys insoluble in sulphuric acid September 30

25461—Roucka, E.—Device for composing of changeable physical or chemical qualities or quantities September 26

*Specifications published this Week*

140439—Nitrogen Corporation—Production of ammonia.

145073—Krause, G. A—Process and means for the evaporation or in insipissation of solutions, and also for effecting chemical reactions.

169247—Naef, E. E—Manufacture of nickel and nickel salts.

169264—Audianne, P—Apparatus for the manufacture of sulphuric anhydride

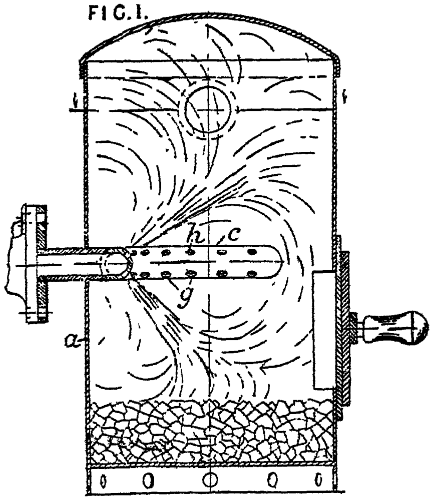
169301—Howorth, F W—Process for the preparation of alumina from clay

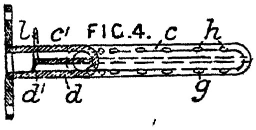
169323—Kernot, J C and British Glues and Chemicals, Ltd—Production of fertilizers

*Abstract Published this Week*

*Sulphur Burners.*—Patent No. 166961—An improved sulphur burning furnace has been Patented by Mr T. A Clayton, of 48, Rue de la Victoire, Paris The air for combustion is supplied in divergent streams and the air supply nozzles are arranged to leave an unobstructed passage for the introduction of sulphur Fig. 1 shows the nozzles arranged in series *h*, *g*, in a hose-shaped pipe *c*, which conforms to the shape of the furnace walls *a* and leaves a central passage for the sulphur introduced from a hopper in the furnace crown. The air streams are individually regulable by a hinged valve *dl*, operated by a lever, the valve admitting air to either side of a partition *cl*, which separates the nozzles *h*, *g* In a modification, a straight pipe *c*, which is disposed in the lower part

FIG. 1.




of the furnace and in proximity to a vertical furnace wall, is provided with divergent nozzles *h*, *g*, and regulation of the air streams is effected by a ported rotary sleeve Partial and complete combustion are ensured by the lower and upper air streams respectively, and sublimation is consequently prevented

Messrs Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each

THE CHEMICAL NEWS.
VOL. CXXIII., No. 3211.

# CHEMICAL REACTIONS ON SURFACES.*

By IRVING LANGMUIR.

AFTER the discovery of the law of mass action, and its kinetic interpretation, it was at first taken for granted that the same principle would apply unaltered to heterogeneous reactions; that is, it was assumed that the reaction velocity of a substance in contact with a solid would be proportional to the concentration of one or more of the reacting substances. Subsequent work showed that other factors than the mere mass action effect were important in determining the velocity of these reactions.

It was shown by Noyes and Whitney (*Z. Physik. Chem.*, 1897, xxiii., 689) that the rate of solution of solid substances in liquids is often limited by the rate of diffusion of the dissolved substances away from the surface. At this surface, therefore, the solution remains practically saturated at all times.

Nernst extended this theory to cover heterogeneous reactions in general. He assumed that all solid surfaces were covered with adsorbed films, and that the reacting substances must diffuse through these films before coming in contact with the underlying metal or other substance, constituting the solid. He assumed that in general the rate of reaction was limited by this diffusion, and that the reaction would be practically instantaneous if it were not for the adsorbed film.

Bodenstein and Fink (*Z. physik. Chem.*, 1907, lx., 46) adopted the general features of this theory, but considered that the film varied in thickness, depending upon the partial pressure of the gases in contact with the solid. In this way they were able to account for cases where the reaction velocity is not proportional to the concentrations of the reacting substances. For example, it was found experimentally that the velocity of the oxidation of sulphur dioxide with a platinum catalyser, as in the "contact process", was inversely proportional to the square root of the pressure of the sulphur trioxide. They explained this by assuming that the platinum was covered by an adsorbed film of $SO_3$, whose thickness was proportional to the square root of the pressure of this component.

Although this theory suggests a possible mechanism for the effect of catalytic poisons, it has not proved to be a satisfactory general theory of catalytic action. Thus, there is no logical reason for assuming, in some reactions, that the adsorbed film is proportional to the square root of the pressure, while in other reactions, it is proportional to the first power of the pressure.

These theories of diffusion through films require the existence of films relatively thick in proportion to the dimensions of molecules, for we find experimentally that the reaction velocities can vary a thousand, if not a millionfold, in reactions when we have to account for this change by a variation in the thickness of a film. In such cases it would be necessary to have films so thick that we should be able to see them. Fink, however, measured the amount of $SO_3$ adsorbed by the platinum per unit area, and found it to be of the order of magnitude of a single layer of molecules. It is, then, hardly logical to assume that the thickness of this film can vary in proportion with the square root of the pressure for a wide range of pressures.

*Evidence for the Existence of very Stable Adsorbed Films.*—Experiments which the writer began in 1912 showed that the effect of residual gases on the electron emission from heated tungsten filaments in vacuum was generally to decrease the emission, instead of to increase it. Oxygen, or traces of water vapour, had a really remarkable effect in decreasing the current. Thus, at temperatures of about 1900° K., the emission was decreased many thousandfold by pressures of oxygen as low as one bar (one dyne per square centimetre, or approximately $10^{-6}$ atmospheres). It did not seem possible that the oxygen could prevent the emission of the electrons unless it covered in some form the larger part of the surface. This film, however, must have been an extraordinarily stable one, to remain on a filament in such good vacuum at this high temperature. At temperatures even as low as 1000° K. no visible film is formed on the surface of tungsten by introducing oxygen, for the $WO_3$ which is produced distils off and leaves the surface apparently clean.

Since that time a long series of investigations has been made on the effect of low pressures of oxygen in altering the properties of tungsten at high temperatures. All of this work confirms the view that even at the highest temperatures, in the presence of traces of oxygen, the surface of the filament is practically completely covered with a film of oxygen.

Thus, when the filament is heated to 3300° K. and a pressure of oxygen of a few bars is admitted to the bulb, the rate of disappearance of the oxygen shows that about 50 per cent of all the oxygen molecules which strike the filament react with it to form $WO_3$, which distils on to the bulb. Since there are three atoms of oxygen in the molecule of this compound and only two in the oxygen molecule, it is clear that *at least one-half* of the tungsten surface, even at this high temperature, must be covered with oxygen in some form.

The chemical effects of this adsorbed oxygen film are as striking as the effects on the electron emission. If a tungsten filament is heated to 1500° K., or more, in pure, dry hydrogen at low pressure, the hydrogen is gradually dissociated into atoms and the atomic hydrogen is adsorbed by the glass walls of the vessel or reacts with any $WO_3$ which may previously have been distilled on to the bulb. The hydrogen pressure therefore gradually decreases. The effect is entirely prevented by minute traces of oxygen. Thus, if a mixture of oxygen and hydrogen be introduced into a bulb and the filament heated to 1500°, instead of the gases reacting to form water vapour, as they would, in contact with a platinum filament, the oxygen reacts gradually with the tungsten to form $WO_3$. While this is going on, the dissociation of the hydrogen by the filament is entirely prevented, so that finally nearly pure hydrogen remains and the pressure remains constant. After ten or fifteen minutes the pressure

*A Paper read before the Faraday Society

of the oxygen decreases to such a point (a minute fraction of one bar) that it no longer is able to prevent the dissociation of the hydrogen. This, then begins *suddenly* to dissociate, and in a few minutes more all of the hydrogen has disappeared.

The oxygen film on the tungsten surface thus consists of oxygen in a form which cannot react with hydrogen even at 1500°. It certainly does not behave like a layer of either tungsten oxide or of highly compressed oxygen gas. Its chemical properties have been completely modified by its adsorption on the tungsten.

The function of the oxygen in preventing the dissociation of the hydrogen is clearly that of a *catalytic poison*. This effect of the oxygen on tungsten is observed with several other reactions. For example, methane is decomposed by tungsten, giving hydrogen, while the carbon is taken up by the tungsten filament, but if the methane is mixed with oxygen, it is not decomposed until all the oxygen has reacted with the tungsten to form $WO_3$, and it is then decomposed as though no oxygen had been present. The same thing happens with ammonia, which, alone, is decomposed easily by a tungsten filament at 900° K., but in presence of oxygen is not decomposed unless the filament temperature is raised above about 1300° K.

If the electron emission is measured while a mixture of hydrogen and oxygen is in contact with the filament, it is found that the electron emission increases suddenly at the same instant that the dissociation of the hydrogen begins.

The remarkable stability of these oxygen films, as well as the complete change in the chemical properties of the oxygen, gives reason for believing that the surface is covered with individual oxygen atoms chemically combined with the underlying tungsten atoms. This film cannot be regarded as consisting of an oxide of tungsten, nor as atomic oxygen, in the sense in which we think of free oxygen atoms. The oxygen atoms are probably held to the surface by four pairs of electrons, just as the oxygen atom is held to the carbon atom in $CO_2$. The oxygen atoms are thus chemically saturated, but the tungsten atoms are not saturated, so that they are held by strong forces to the tungsten atoms that lie below them. This kind of structure is quite in accord with the conception of the structure of solids to which we are led by the work of the Braggs, on crystal structure.

Work with other metals has shown that stable films of the kind we have just been discussing are of very common occurrence. Oxygen forms a similar film on carbon, and carbon monoxide, hydrogen cyanogen, hydrogen sulphide, phosphine, and arsine form stable films on platinum. It is probable that all substances that have a poisoning effect on catalytic surfaces form films of this kind.

*Evidence that these Stable Films are Monomolecular and that the Molecules tend to be Oriented on the Surface.*—According to our present conceptions, atoms consist of electrons arranged in space about a positively charged nucleus. Whether we assume that the electrons are moving or not, it is certain that the electrons nearly completely surround the nucleus. In most molecules, atoms share pairs of electrons (duplets) with each other. In any electrically neutral molecule, the field of force must decrease in intensity with a very high power of the distance from the centre. Born has calculated that the electric force around a group of eight electrons, arranged at the corners of a cube and surrounding a nucleus having an equivalent charge, is inversely proportional to the tenth power of the distance from the nucleus. Debye, from an entirely different viewpoint, reaches the conclusion that the force of attraction between molecules is inversely proportional to the eighth power of the distance between them. From considerations of this kind, it can be shown that the electric force near the surface of an atom must decrease from a maximum value at the surface to a value one-half as great within a distance of about $0{\cdot}3 \times 10^{-8}$ cm. In fact, an analysis of Debye's and other data shows that this force decreases in about the same way on receding from the surface of the atom, for molecules, of widely differing type. In other words, this distance of $0{\cdot}3 \times 10^{-8}$ is a nearly universal constant, and in this way we get a much better conception of actual conditions close to the surface of an atom than by assuming that the force decreases with the power of the distance.

If magnetic forces exist within the atom it can be readily calculated that these forces must decrease even more rapidly as the distance from the atom increases.

It must be said, therefore, that our present conception of the structure of atoms and molecules makes it impossible for us to conceive of any appreciable force which one atom or molecule can exert directly on others at distances greater than two or three Ångstrom units ($10^{-8}$ cm.). Where effects are transmitted to greater distances than these, it must be the result of a transmission through and by atoms or molecules of matter. In view of the structure of atoms from positive and negative particles, it is clear that atoms should have the properties of a dielectric. Thus, if we have a chain of atoms linked together by duplets—as, for example, in the hydrocarbon chain of an organic compound—and we bring a positively charged body near one end of the chain, the electrons will be attracted and the nuclei repelled, so that a certain displacement of these particles with respect to one another will result. This effect is then transmitted with gradually decreasing intensity from atom to atom throughout the length of the chain, resulting in an accumulation of positive charge at the opposite end of the chain. The chemical evidence indicates clearly that effects of this kind are sometimes transmitted relatively great distances. The many facts which have led some chemists to assume polar valences, such as directed valences in organic compounds, receive a simple explanation on the basis of these transmitted effects.

In cases where atoms are not joined firmly to one another by the sharing of duplets, we should never expect the transmission of electric force to extend through more than about one atom. On this basis, we are led to deny the existence of thick, stable, adsorbed films of gas molecules such as those which were assumed in the Nernst and in the Bodenstein-Fink theory of heterogeneous reactions. If, for example, a surface is covered with a layer of oxygen *molecules*, then there should be little if any more tendency for other molecules to form a second layer than there

would be for these molecules to remain in the surface of liquid oxygen at the same temperature. Thus, only when we have nearly saturated vapours should we ever obtain films of gas molecules which exceed monomolecular thickness.

The general opinion among colloid chemists and others who have worked with adsorption effects, at least up to a few years ago, seems to have been that adsorbed films were usually of a thickness of 100 to 1000 A. According to the views we have reached here, such thick films cannot be regarded as the result of true adsorption, but can result only from condensation in capillary spaces in presence of nearly saturated vapours or are due to sorption or solution. For example, it can be shown that glass, just like glue, can sorb large quantities of water vapour, but this is a real penetration of the water molecules into the solid material and is not a strictly surface action.

There is no good reason for believing that it is only at low pressures and high temperatures that adsorbed films are of monomolecular thickness. The effect of catalytic poisons (as studied for example, by Faraday), surface tension effects, the lubricating properties of thin oil films, passivity phenomena in electrochemical actions, electrolytic overvoltage, &c., all point unmistakably to the existence at atmospheric pressure of stable films quite analogous to those observed in high vacuum and at high temperatures.

Lord Rayleigh, in 1899, on the basis of some beautiful experiments on surface tension, showed that the film of olive oil on water contaminated with this substance has a thickness of 10 A., and is therefore probably of monomolecular thickness. This work was later extended by Devaux, Labrouste, and others. These results were of particular interest to the writer, because of their important bearing on the question of the range of atomic and molecular forces and the structure of adsorbed films in general.

Experimental results on the spreading of oils on water surfaces have completely confirmed the views outlined above. The only oils which spread on water are those whose molecules have active groups, such as the —COOH, —OH, &c, which normally increase the solubility of a substance in water. The spreading therefore occurs because the active group has an affinity for water, while the hydrocarbon chain tends to remain in contact with other chains of the same kind. The molecules on the surface must, therefore be *oriented,* so that the actual surface consists of the hydrocarbon part of the molecules, while the active groups are all turned downward towards the surface of the water. It is evident that if we have a series of substances having the same active group, but different lengths of hydrocarbon chain, the number of molecules per unit area in the oil film should remain about constant, while the length of the molecule in the vertical direction, and therefore the thickness of the film, should increase in proportion to the length of the hydrocarbon chain. Numerous experiments have completely verified these theoretical deductions (Langmuir, *Met. Chem. Eng.,* 1916, xv., 468; *Jour. Amer. Chem. Soc.,* 1917, xxxix., 1848. A brief summary was published in *Trans. Faraday Society,* 1920, xv., 1). In this way it becomes possible to measure the lengths and cross-sections of the molecules of oil films on surfaces, and to prove conclusively that the films are not only monomolecular, but that orientation of the molecules is a factor of vital importance in their formation. Very accurate measurements of the forces involved in the formation of these films and valuable additional information in regard to their structural changes have recently been obtained in England by N. K. Adam (*Proc. Roy. Soc.,* 1921, xcix., 336).

Evidence that surface films are monomolecular and that the molecules are oriented is also obtained from surface tension data on pure liquids. While the spreading of oil films on water depends upon the most active group in the molecule, the surface tension of a liquid—which is a measure of the potential energy of its surface—depends primarily on the least active group in the molecule, for the group with the lowest stray field of force will tend to form the actual surface layer, in order to make the potential energy a minimum. An analysis of practically all available published data on surface tension leads to a verification of this hypothesis.

The interfacial surface tension between two liquids, such as water and mercury, or water and oil, gives, as W. B. Hardy has shown, a measure of the energy changes involved in the formation of the interface. W. D. Harkins (*Jour. Amer. Chem. Soc.,* 1917, xxxix., 354, 541) has made numerous measurements of interfacial surface tensions which show that the work done in the formation of such interfaces is a measure of the activity of the most active part of the molecule, for the molecules become oriented at the interface.

A fourth method of determining the thickness of surface films and proving that they are oriented in the surface, depends upon the use of Gibb's thermodynamic equation, giving the total amount of material adsorbed in the surface of a solution in terms of the change in the surface tension of the solution as the concentration of the solute is altered. By measuring the surface tension of solutions at various concentrations it is thus possible to determine the amount of material adsorbed per unit area. As the concentration is increased, the amount adsorbed increases and approaches a definite limit. The results show that in all such cases the maximum amount adsorbed corresponds to that in a monomolecular film. It is thus possible to determine the number of molecules adsorbed per unit area and thus find the cross-section of the molecules. The length is then obtained from the known volume of the film. This method is applicable to adsorbed films on liquids formed either from substances dissolved in the liquids, or from substances present as vapour above the liquid. When a solution has a lower surface tension than the pure solvent, the surface has a monomolecular film of the dissolved substance, but where the solution has a higher surface tension than the solvent the surface of the solution consists of a monomolecular film containing nothing but pure solvent.

Direct experiments have also been made by the writer to determine the maximum amount of gases that can be adsorbed by plane surfaces of glass, mica, and platinum (*Jour. Amer. Chem. Soc.,* 1918, xl., 1361). At ordinary temperatures with pressures of nitrogen, hydrogen, argon, carbon dioxide, &c., up to a few hundred bars, at

least, there is no measurable adsorption by glass or mica—that is, less than 1 per cent of the surface is covered by a single layer of molecules. At the temperature of liquid air, however, and at pressures of the order of a hundred bars, the surfaces become saturated by an adsorbed film which never exceeds one molecule in thickness. The evidence is that these films consist of *molecules* and that primary valences are not involved in their formation. The forces involved are unquestionably the result of the stray field of force around the molecule, and involve no radical rearrangement of the electrons. The forces are probably very much like those involved in the formation of substances containing water of crystallisation or ammonia of crystallisation.

With a clean platinum surface which had been made catalytically active by bringing it into contact with a mixture of oxygen and hydrogen at low pressures, at a temperature of about 300° C., the adsorption phenomena were totally different from those observed with glass and mica, at least in the case of the gases hydrogen, oxygen,. and carbon monoxide. When small amounts of oxygen were allowed to come in contact with the platinum surface, the oxygen disappeared almost instantly, until the total amount adsorbed corresponded to a monomolecular or monatomic film, and then no further amount of this gas could be adsorbed, even with a great increase in pressure. No trace of the oxygen could be pumped off by heating the platinum in the best vacuum to 360°.

If the platinum in this condition was allowed to come in contact with hydrogen or carbon monoxide at low pressure, the oxygen film was removed and water vapour or carbon dioxide was produced, even at room temperature, and then an additional amount of hydrogen or carbon monoxide was adsorbed sufficient to produce a monomolecular film of these substances. The carbon monoxide film could be very gradually pumped off at a temperature above 300°. No measurable amounts of nitrogen or carbon dioxide were adsorbed by the platinum at any time.

These remarkably stable films on the platinum surface are of the same type as the oxygen films adsorbed on tungsten surfaces. Primary valences are unquestionably involved in their formation. In the case of the carbon monoxide, the carbon atom must be directly attached to the platinum, while the oxygen is thus above the carbon. The carbon monoxide molecules—if we can so speak of them—are thus oriented on the surface, very much as the molecules in an oil film. The experiments with platinum give a direct proof that these stable films are of monomolecular thickness.

The evidence for the existence of monomolecular films is thus by no means confined to experiments at low pressures for equally striking evidence furnished by the surface tension phenomena. The orientation of molecules in surface layers follows as a necessary result from the conclusion that the range of atomic and molecular forces is of the order of 1 Å. The orientation in surface films is a phenomenon with which we must constantly reckon, just as we must consider structural relationships in the molecules of organic compounds. Of course, there are cases where the adsorbed film consists of single atoms, or of various symmetrical molecules, such as $CH_4$ or $CCl_4$, where we do not need to consider orientation. But wherever different parts of the surface of a molecule may be assumed to have different properties, we must take into account the probability of orientation in all adsorption phenomena and therefore in all catalytic actions on surfaces.

*Mechanism of Adsorption.*—We have discussed the structure of adsorbed films and the forces involved. Let us now consider the mechanism by which these films form on a surface or disappear from the surface.

When the adsorbed film of carbon monoxide on platinum gradually disappears, on heating the metal to 300° in the highest vacuum, it is logical to look upon this as an evaporation process. When a filament of platinum, or tungsten, or other metal is heated to a sufficiently high temperature in vacuum the material evaporates. If the metal is placed in a uniformly heated enclosure, the evaporation from the surface—which we may consider continues unchanged—will be gradually offset by the return of atoms of metal from the vapour which accumulates in the space Finally, an equilibrium is reached in which the rate of condensation of the vapour is equal to the rate of evaporation.

If we can assume that all the atoms of the vapour which strike the surface of the metal condense on the first collision, we may calculate the rate of condensation from the vapour pressure by means of the kinetic theory of gases. The formula usually given for the rate of effusion of gases through small openings can readily be put in the form

$$m = \sqrt{\frac{M}{2\pi RT}}p$$

where M is the molecular weight of the vapour, R is the gas constant, $p$ is the pressure of the vapour, and $m$ is the rate at which the gas molecules strike against the surface, in grms. of vapour per square centimetre per second. Expressing $p$ in bars, and placing $R = 83{\cdot}15 \times 10^6$ ergs per degree, this reduces to

$$m = 43\ 74 \times 10^{-6}\sqrt{\frac{M}{T}}p.$$

This equation gives the rate at which the molecules of a vapour strike against the surface. If every molecule condenses, and if we have equilibrium, then the rate of evaporation must also be given by this equation, so that we obtain a direct relation between the vapour pressure of a substance and its rate of evaporation in perfect vacuum.

Experiments with many different metals have shown close agreement between the vapour pressures determined in this way from the rate of evaporation and the vapour pressures measured by processes which involve the formation of saturated vapours. Knudsen has made careful experiments of this kind with mercury vapour, while A. S. Egerton (*Phil. Mag.*, 1917, xxxiii., 33) has carried out work with cadmium and zinc. Their results indicate that every atom of vapour condenses

Knudsen and R. W. Wood independently arrived at the conclusion that mercury or cadmium atoms condensed on a glass surface only if this surface is cooled below a certain critical temperature. Below this temperature, practically

every atom is supposed to condense, while at temperatures materially above this critical point not one atom, out of thousands which strike the surface, condenses. This conclusion is not only inherently improbable in many ways, but it not capable of accounting for numerous experimental facts. Wood's and Knudsen's experiments are better explained by assuming that all the atoms of cadmium and mercury which strike a glass surface even at high temperature, condense on the surface, but that at temperatures above the "critical temperature," the atoms re-evaporate before they have a chance to be struck by other atoms of the vapour. The writer has discussed this question in detail in a paper in the *Physical Review*, 1916, viii., 149, and subsequently carried on experiments with cadmium vapour (*Proc. Nat. Acad. Sci.*, 1917, iii., 141) which demonstrate conclusively that cadmium atoms evaporate rapidly from a clean glass surface at room temperature There is no real reason for believing that cadmium may not also evaporate from glass at temperatures only slightly above the critical temperature of $-90°$ C. cited by Wood. Since molten cadmium does not wet glass it is clear that the forces between a cadmium atom and a glass surface are much less than between cadmium atoms, and the rate of evaporation should therefore be much higher.

In most cases of adsorption we are dealing with a solid surface having a strong field of force, or a high potential energy per unit area, while on this solid is condensed a substance whose molecules possess a rather weak stray field of force. These are the conditions when ordinary gases condense on cooled surfaces of glass or metals. The forces which might tend to hold a second layer of molecules are so weak that evaporation from the second layer occurs at a rate high compared with that from the first. Only with nearly saturated vapours, then, can a second layer form.

With cadmium and mercury vapours condensing on glass, however, we have a case in which the evaporation from the second layer takes place much more slowly than from the second layer. We see, therefore, that a kind of instability necessarily results. There is considerable difficulty in getting the first layer to form, because the atoms tend to evaporate before the others are able to condense on top of them or beside them. If the first layer ever does form, then the evaporation practically ceases and successive layers are then formed with ease. This view seems to give a clear picture of the mechanism of the formation of nuclei on which condensation occurs. The formation of frost crystals on a greasy window-pane, or Moser's breath figures on glass, are illustrations of effects of this kind

We might suppose that when molecules of a gas strike a surface, only a certain fraction $a$ condense on the surface, while the others are reflected. Experimentally, however, it seems hard to find examples where $a$ is appreciably different from unity. Soddy, Knudsen, and others have found, however, that in heat conduction from a solid surface to a gas at low pressure, the gas molecules which strike the surface do not always reach thermal equilibrium with the surface before leaving it. Knudsen has given the name "accommodation coefficient" to the fraction which expresses the actual heat conduction to that calculated on the assumption of heat equilibrium. It is to be noted, however, that these coefficients are usually of the order of magnitude of 0·8, and they are determined under conditions in which the rate of evaporation of the gas from the surface is unusually high. We should probably, therefore, look upon these as rather exceptional cases, and, unless we have definite evidence to the contrary, should assume that the coefficient $a$ is unity.

When gas molecules of any kind strike a surface, we should therefore not expect them to rebound elastically, but rather expect them to condense. Adsorption is thus the result of the time lag between condensation and evaporation. In some cases the rate of evaporation is so low that evaporation practically never occurs. This is what happens, for example, when a catalyst is poisoned by sulphur or arsenic compounds. In other cases, the rate of evaporation may be so high that the time that elapses between condensation and evaporation may be of the order of $10^{-12}$ seconds or even less.

*The Mechanism of Chemical Reactions on Surfaces.*—The clean surface of a solid crystalline body must consist of atoms or molecules arranged in a surface lattice, or kind of checkerboard. Non-crystalline bodies, such as glass, must have surfaces in which the atoms are probably not in regular lattices. We may also have surfaces which are porous, or consist of irregular filamentary projections and interlocking chains of atoms or molecules. In such cases the extent of the surface cannot be defined, except in a purely arbitrary manner. Most finely divided catalysts, such as platinum black, or activated charcoal, &c., must have structures of great complexity, and it is probable that the atoms are attached to each other in the form of branching chains so that there are hardly any groups of as little as three or four atoms which are as closely packed as they would be in the crystalline solid. In order to simplify our theoretical consideration of reactions on surfaces, let us confine our attention mainly to reactions on plane surfaces. If the principles in this case are well understood, it should then be possible to extend the theory to the case of porous bodies.

In general, we should look upon the surface of a catalyst as consisting of a checkerboard in which some of the spaces are vacant, while others are filled with atoms or molecules. Some of these molecules, or atoms, may be so firmly attached that they do not evaporate at an appreciable rate. Others leave the surface from time to time, and the vacant spaces thus left are sooner or later filled by other molecules which strike the surface and condense.

If we have a surface such as that of platinum, and we allow to come in contact with it a gas, which forms an adsorbed film that evaporates slowly, or not at all, the surface is no longer a platinum surface as far as possible interaction with other gas molecules is concerned. The catalytic activity of the platinum has thus been lost, or the catalyst has been poisoned. Arsenic, sulphur, or phosphorus compounds have this effect, for the atoms of these elements presumably combine directly with the atoms of the platinum and do not evaporate at an appreciable rate. Cyanogen and carbon monoxide have a similar, but more transient effect on platinum, only as

long as these gases remain present in the gas phase does the poisoning influence persist.

Faraday studied the effect of various substances in poisoning the catalytic activity of platinum on the reaction between oxygen and hydrogen By boiling platinum foil in concentrated sulphuric acid, and then washing with distilled water, it is brought into a condition where it brings about the combination of oxygen and hydrogen at room temperature. The presence of carbon dioxide did not retard this action, but a trace of carbon monoxide stopped the action entirely, although on placing the platinum in a mixture of fresh gas, free from monoxide, the reaction proceeded in a normal manner. Hydrogen sulphide, or arsine, not only prevented the action while they were present, but produced a permanent alteration in the platinum, so that it was necessary to boil it again in acid before it could be made active. The poisoning effect of oxygen on the catalytic activity of tungsten at high temperature is of the transient kind produced by carbon monoxide on platinum.

In the presence of a gas which has a poisoning effect on a catalyst, the reaction velocity depends on that fraction of the surface which is *not* covered by molecules of this gas. If the temperature is high enough and the catalyst poison is of the kind that has a transient effect, the adsorbed molecules evaporate at a certain rate. If much of the gas is present, the vacant spaces thus produced tend to be refilled by these molecules. The fraction of the surface which is in an active condition is thus directly proportional to the rate of evaporation of the film, and inversely proportional to the partial pressure of the gas producing the poisoning effect. We are thus led to an understanding of the mechanism of the type of reaction which was explained by Bodenstein and Fink by assuming adsorbed films having a thickness varying in proportion to the pressure of the gas.

When gas molecules condense on a solid surface in such a way that they are held on the surface by primary valence forces, involving a rearrangement of their electrons, their chemical properties become completely modified. It is not surprising, therefore, that in some cases such adsorbed films should be extremely reactive, while in other cases they may be very inert to outside influences. Thus oxygen adsorbed on platinum reacts readily with hydrogen or carbon monoxide, while oxygen on tungsten, or carbon monoxide on platinum, show very little tendency to react with gases brought into contact with their surfaces. The specific nature of the behaviour of these various films is quite consistent with the theory that the adsorption depends on typical chemical action. In many cases, especially where we deal with adsorption of large molecules, the orientation of the molecules on the surface is a factor of vital importance in determining the activity of the surface towards reacting gases.

The reaction which takes place at the surface of a catalyst may occur by interaction between molecules or atoms adsorbed in adjacent spaces on the surface, or it may occur between an adorbed film and the atoms of the underlying solid, or again, it may take place directly as a result of a collision between a gas molecule and an adsorbed molecule or atom on the surface. This third kind of action is perhaps indistinguishable from one in which the incident gas molecules condense on top of those already on the surface, and then react with them before they have a chance to evaporate.

When a surface is covered by different kinds of adsorbed molecules distributed at random over the surface, we may expect in general that adsorbed molecules in adjacent spaces should be able to react with one another at a rate which is proportional to the chance that the given molecules shall lie in adjacent spaces. This kind of mechanism has been discussed at length by the writer in connection with a study of the dissociation of hydrogen in contact with a tungsten filament (*Jour. Amer. Chem. Soc.*, 1916, xxxviii., 1145). When the hydrogen molecule strikes a tungsten surface at high temperature, at least 68 per cent of the molecules condense on the surface and are held there as individual atoms. After the action has proceeded for a time, the distribution of atomic hydrogen over the surface is given by the probability laws.

(To be continued).

## THE NEW INTERNATIONAL COMMISSION ON CHEMICAL ELEMENTS.

Remarks by Prof BOHUSLAV BRAUNER, Ph.D., Hon.D.Sc.(Manc.)

The report of the meeting of the International Conference of Pure and Applied Chemistry, held at Brussels at the end of June, published in *Nature* of August 18 (p. 787), contains the following statement: "It was felt that the exact determination of atomic weights and their publication to several places of decimals has now *lost a good deal of its scientific signification* in view of the work of Dr. Aston and others, and that exact *atomic weights are now becoming factors of analytical calculation rather than features of a chemical analysis* . . . . The atomic weights—often representing merely the average mixture of isotopes—will be of practical rather than theoretical interest, &c."

The official report, which I obtained as a member of the new "International Commission on Chemical Elements" (consisting of two Honorary Presidents and seven Members) sounds a little differently. According to it, Sir William Pope remarked that "work of all kinds is modifying the fundamental notion of the chemical element, and so the constitution (establishment) of the Table of Atomic Weights does not present the same interest as it presented at the epoch when atomic weights were regarded as absolute constants." Therefore, a new Commission, with a larger programme (Table of Radioactive elements, isotopes, and atomic masses) was proposed and really constituted.

Every chemist will undoubtedly agree with Sir W. Pope, and will welcome his proposition and the formation of the new Commission. On the other hand, it does not seem possible for me to accept the principle, as reported in *Nature*, especially that "exact atomic weights are now becoming factors of an analytical calculation rather than features of a chemical hypothesis."

I beg to remark that we know to-day two kinds of isotopes, which we may call A and B. The

isotopes A are either radioactive elements (heads) or products of the same or different series of radioactive disintegration, Soddy's isotopes. The isotopes B, J. J. Thomson's and Aston's isotopes, represent mixtures of extremely similar elements, which were formerly regarded as one individual element.

The isotopes A descend from U or Th down to the isotopes of Tl, and the different series end in "leads" of the atomic weights 206 and 208, but all isotopes representing one place do not necessarily occur together at the same time, *e.g.*, the 7 or 8 isotopes of lead (Moseley's atomic number 82).

The isotopes B, as far as we know, *always* occur in nature together, and *always* in the same proportions, their mixture yielding *always* the same average *combining weight*. Dr. Aston has shown that they can be separated from their mixtures by suitable electro-magnetic analysis and that their *atomic masses* are represented by integers (O=16, which standard was recommended for the first time *with success* by the writer in CHEMICAL NEWS, 1888, lviii., 307). They go to-day from H up to Cs.

Dr. Aston has shown that, besides the mixtures of isotopes also *pure elements* exist. Their atomic *masses* are also integers, their *atomic weights* as determined by the most able human hands by means of the *balance* show in the majority small, but real deviations from integers.

We know up to the present the following "pure" elements: H=1·008, He=4·00, C=12·005, N=14·008, O=16·000..., F=19·00, Na=23·00, P=31·04, S=32·06, As=74·96, I=126·92, Cs=132·81 (?). These are their *atomic weights*, which we must not confound with their *atomic masses*: 4, 12, 14, 16, 19, 23, 31, 32, 75, 127, and 133.

As regards the question, what theoretical interest present our atomic weights, it must be admitted that the original form of the Periodic Law, as given by Mendeléef in 1871: "The properties of elements, etc., are periodic functions of their atomic weights" had to be changed as soon as it was definitely proposed by the writer that the "combining weight" of tellurium is higher than that of iodine, and, in fact, it was also pointed out that our tellurium cannot be a simple substance of a homogeneous body, for, if such an *element* possessed the high *atomic weight* (Te=127·6, I=126·9) "the Periodic Law would lose a great deal, if not all, of its authority" (*Chem. Soc. Trans.*, 1889, lv., 706, 709). On the contrary, it was assumed that "tellurium with the combining weight of 127·6 is a true 'gadolinium' of the hydrogen sulphide group,", *i.e.*, an inseparable mixture of very similar elements. I regret that Dr. Aston has not yet succeeded in proving it.

We also know to-day, that owing to the anomalies Te>I, Co>Ni, and A>K, as well as owing to the discovery of the isotopes and, as pointed out by the author about the series of 13 rare-earth elements, from Pr=140·9 up to Lu=175·0, the properties, etc., of which are *not* periodic functions of their atomic weight (see Abegg's "Handbuch III., i., pp. 171, 261, 275, 283, 304) the properties of elements and their compounds (except those of the rare-earths) are functions of Moseley's or atomic numbers. But I would beg to add that the original formulation of Mendeléef's Periodic Law is not entirely invalid, and that the properties of the *pure* elements, *i.e.*, of those which do not possess any isotopes, are still periodic functions of their atomic weights. It is true that since the discovery of isotopes, the constitution of the Table of Atomic Weights does not present the same interest as it presented at the epoch when atomic weights were regarded as absolute constants, but some of the numbers have gained a fresh theoretical interest, as I would like to prove.

Our elementary atoms are peculiar condensations of hydrogen nuclei (protons or positive electrons) or helium nuclei, which are in their turn again condensation of hydrogen nuclei, and probably also of $H_3$ nuclei and of electrons.

As regards the mechanical masses of the inner and the outer negative electrons in the atoms, it is a question whether they possess any mass at all, considering that their position in the atoms is rather stationary and under quite different conditions from those under which their *electro-magnetic mass* was determined (*i.e.*, from their rapid motion in cathode rays). At least the fact, that Aston's *atomic masses* are integers, would rather show that the masses of electrons are negligible

Now the question arises: why do we find with our chemical processes and the balance that the *atomic weights* of the *pure* elements C, N, P, S, are *larger* than their *atomic masses*, why those of As, I, and Cs are *smaller* and why those of He, O, F, Na, are exactly equal to their *atomic masses*, or in other words, why is the hypothesis of Prout in its modern form valid for atomic masses but only in four out of twelve cases for the corresponding atomic *weights*? Another interesting question arises: why are Aston's isotopes B, as far as we know, always mixed up in the same proportion?

I do not think that, say only an American chemist might find the *combining weight* (average atomic weight) of chlorine 35·46 and of silver 107·88, and that an Australian may find from another material occurring in nature Cl=35·1, and Ag=107·5, as some chemists seem to be afraid of. I might only remind them of the experiments of Harkins, who, after many troublesome processes effected only a slight separation of the isotopes of chlorine. And if such a difference should be found one day, it will require the work and authority of an experienced chemist, who has formerly made reliable, exact atomic weight determinations to prove that such a great and sensational discovery was really made.

Readers of the CHEMICAL NEWS have undoubtedly perused the most interesting Presidential Address given by Sir T. E. Thorpe to the recent meeting of the British Association at Edinburgh, in which the modern views on atoms, &c., were discussed (CHEMICAL NEWS, Sept. 9 and 16, 1921). I am very glad to find the following passage: "The term 'atomic weight' has thus acquired for the chemist an altogether *new and much wider significance*. It has long been recognised that it has a far deeper import than as a *constant useful in chemical arithmetics*"; and further that he recommends to "determine with the highest attainable accuracy the departures from the whole number rule."

I quote those few words of an authority possessing great experience in questions regarding atomic weights, with great pleasure and satisfaction, for they show that my opposition to the views quoted at the beginning of this article is not unfounded.

I beg to conclude with an historical reminiscence. J. S. Stas, who was originally an adherent of the hypothesis of Dr. Prout (1815), concluded from his own work, published in 1860-1865, that it is untenable because the atomic weight of the 11 elements cannot be expressed by a whole number, and the atomic weight of chlorine, Cl=35·457 (O=16) is far from being a multiple of 1 or 0·5 or 0·25 as might be expected from the point of view of Dumas' modification of Prout's hypothesis. Stas declares the latter as "a pure illusion."

A great contemporary of Stas, Charles de Marignac, another great authority in atomic weight determinations, has shown ("Œuvres Complètes," I., 1860, 693; II., 1865, 281), that it cannot be due to a mere chance that eight out of nine atomic weights determined by Stas differ from whole numbers only by ±0·068, instead of about ±0·5, as expected by the calculus of probability. Marignac points out that the fundamental principle which led Prout to establish his law, ***the idea of the unity of matter***, is something higher than the search for the common division of the atomic weights, and he adds the following prophetic words (I., 701): "Could we not suppose that the cause, unknown but probably different from the chemical and physical agencies, which has determined certain groupings of the atoms of the unique primordial matter in such a manner as to give birth to our simple chemical atoms, and to impress to each of these groups a special character and particular properties, could at the same time exercise an influence upon the manner according to which these groups of atoms obey the law of universal attraction, of such a kind ***that the weight of each of them is not exactly the sum of the primordial atoms which constitute it***?

A still more decided belief in the compound nature of our elements was expressed by Marignac in a public lecture given by him in Geneva in January, 1866, "Sur l'hypothèse de l'unité de la matière," and published only recently by Ph. A. Guge in his *Journ. Chim. Phys.*, J. 18, No. 3, October, 1920.

Mendeléef, who never admitted that his Periodic System points to the unity of matter, expressed in spite of this in his classical paper on the Periodic Law (*Ann. Supl.*, Bd. 8, 1871) a similar idea. Even if we admit that the matter of the "elements is perfectly uniform (homogeneous), there is ***no reason to assume that n-parts by weight*** of one element or of *n*-atoms, in the case of a transmutation into the atom of another element ***will be n-times heavier than that of the first one.*** The law of the conservation of weight can be regarded as a special case of the conservation of energy or of motions. The weight is probably caused by a peculiar motion of matter and there is no reason to refuse the possibility of the conversion of these movements in the case of a formation of elementary atoms into chemical energy or into another form of motion."

Both these great chemists have predicted what we accept to-day that $4\times1{\cdot}008+(2e \text{ inner})+2e$ outer)$=4{\cdot}00=$He. I may be allowed to remark that whenever I tried to ask Mendeléef what was his (then) opinion on this subject he invariably evaded this topic, for until his death he held the view that elements are true "individuals" from (−) eternity to (+) eternity!

*Conclusion.*

I recommend the new International Commission to adopt the following nomenclature:—

(1) *Atomic Masses* only for the whole numbers of the isotopes B, as determined ***physically*** by Dr. Aston's method.

(2) *Atomic Weights.* This term justified by its historical and wide-spread use should be applied for the numbers as obtained by ***chemical methods*** and by the use of the ***balance,*** no distinction being made between ***pure*** elements, mixtures of isotopes or single isotopes.

Accordingly I beg to propose to call the Sub-Committee of the "International Commission on Chemical Elements" a "Sub-Committee for *Atomic Weights.*"

Chemical Laboratory,
Bohemian University, Prague.
October 1, 1921.

## VOLUMETRIC ESTIMATION OF MIXTURES OF PERMANGANATE, DICHROMATE, AND CHROMIC SALTS.

By NITYA GOPAL CHATTERJI, M.Sc.

(1) *Estimation of a Mixture of Permanganate and Dichromate.*

THE method is an extension of the well-known method of Volhard for the volumetric estimation of manganese. It depends upon the fact that a solution of permanganate can be easily and completely removed as insoluble hydrated manganese dioxide by the addition of a mixture of solutions of manganese sulphate and zinc sulphate Instead of zinc sulphate, a soluble salt of magnesium, calcium, or strontium can be used. We have reasons to believe that the action of these salts is primarily to coagulate the colloidal manganese dioxide formed by the interaction of permanganate and manganese sulphate, though Volhard and others believe that the zinc sulphate or oxide forms an insoluble manganite.

*Procedure.*—The mixture of permanaganate and dichromate is first titrated against a standard solution of ferrous sulphate, the end point being easily marked by the appearance of a permanent dirty pink colour. From this the total iron equivalent of the mixture is obtained. Now 20 or 25 cc. of the original mixture is taken, and to it is added slowly a hot solution of manganese and zinc sulphates with constant shaking until the pinkish tinge of the permanganate is no longer visible. To ensure complete decomposition of the permanganate, a slight excess of the sulphate solution is added. Filter off the precipitate of hydrated manganese dioxide, wash thoroughly with hot water containing a little dilute sulphuric acid, and make up the filtrate and washings to a known volume. Find out the strength of the dichromate solution contained in the filtrate by direct titration with standard ferrous sulphate solution.

(2) *Estimation of Mixtures of (a) Dichromate and Chromic Salt, and (b) Permanganate and Chromic Salt.*

The estimation of these mixtures depends upon the fact that a solution of a chromic salt is completely oxidised to dichromate by heating an acidulated solution of it with hydrated manganese dioxide prepared in a special manner.

*Preparation of the Hydrated Manganese Dioxide.*—A solution of pure manganese sulphate is placed in a large porcelain dish and a few grms. of potassium or sodium nitrate are added to it and the mixture heated. Drop by drop a solution of potassium permanganate is added, and the mixture is vigorously stirred. The addition of the permanganate is continued till there is a very slight excess of it. The precipitate is filtered and washed free from electrolytes with hot water. The substance is then dried at 40-45° C., and kept in a stoppered bottle. It is of a dark-brown colour.

*Procedure.*—(*a*) *Permanganate and Chromic Salt.*—Take 20 or 25 cc. of the mixed solution, add to it about a grm. of the manganese dioxide and a few drops of dilute sulphuric acid, and boil for two or three minutes. Filter, wash, and make up the filtrate to a known volume together with the washings. Find out the strength of the filtrate by titrating a standard solution of ferrous sulphate. This gives the iron equivalent of the mixed solution. Take another quantity of 20 or 25 cc. of the mixed solution, heat and add slowly a mixture of manganese and zinc sulphates with constant shaking till the colour of the permanganate is no longer visible. Add a slight excess of the sulphate solutions, about half a grm. of hydrated manganese dioxide, and boil for a few minutes. Filter and wash, and make up the filtrate and washings to a known volume. (Usually the manganese dioxide precipitated by the decomposition of the permanganate is found to be sufficient for the oxidation of the chromic salt, but it is better to add an excess of the oxidising agent.) Find the strength of the filtrate by titrating against a standard ferrous sulphate solution. This gives the iron equivalent of the chromic salt solution, and the difference between the first and second titrations gives the strength of the permanganate solution.

(*b*) *Dichromate and Chromic Salt.*—The amount of the dichromate is first determined by titration against a standard ferrous sulphate solution. A known quantity of the mixed solution is then oxidised by hydrated manganese dioxide, filtered and washed, and the strength of the filtrate determined in the usual manner. This gives the total amount of the dichromate and chromic salt, and hence the difference between the second and the first titrations gives the amount of the chromic salt.

The method seems capable of being applied for the determination of chromium and manganese in steel, to investigate which experiments are being carried on.

Research Department,
Government Technological Institute,
Cawnpore (India).
September 14, 1921.

# THE SOLUBILITY OF PHTHALIC ACID IN WATER AND SODIUM SULPHATE SOLUTIONS.

By L. McMASTER, E. BENDER and E WEIL.

THE purpose in undertaking this work was to determine the solubility of phthalic acid in water and in sodium sulphate solutions of different concentrations at different temperatures, because the literature records but few facts concerning the solubility of phthalic acid. Vaubel (*J. prakt. Chem.*, 1895, (2), lii., 72; 1899, lix., 30) gives the solubility of phthalic acid in water at 14° as 0·54 grm. per 100 grm. of solution. Graebe (*Ann.*, 1887, ccxxxviii., 321) gives its solubility at 99° as 18 grm. per 100 grm. of solution. In the preparation of phthalic acid it is often set free by treating its sodium salt with sulphuric acid and it was for this reason that its solubility was determined in sodium sulphate solutions. These solutions were made up to be 10 and 15 per cent by weight.

The purity of the phthalic acid used was from 99·95 per cent, with 0·02 per cent ash, to 100 per cent. No attempt was made to purify the acid further. It was supplied by the Monsanto Chemical Works Pure anhydrous sodium sulphate was used. All solutions were prepared with water from which the carbon dioxide had been removed.

*Experimental.*

The method followed was somewhat similar to that of Walton and Judd (*Jour. Amer. Chem. Soc.*, 1911, xxxiii., 1036). The acid was put into 175×55 mm. heavy-wall glass tubes with the water or sodium sulphate solutions, and agitated until equilibrium was attained. The tubes were immersed in a constant temperature water-bath, which was controlled by a mercury-column regu-

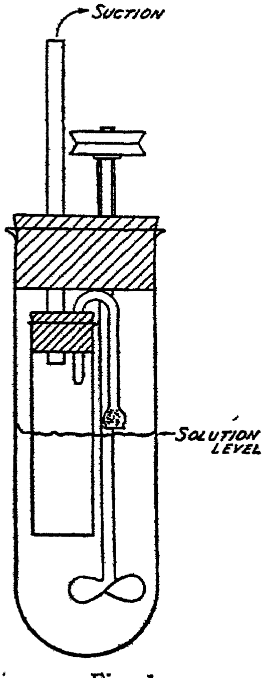



Fig. 1.

lator. At 25° a standardized thermometer reading from the −10° to +32° and graduated in 0·02° was used. For the higher temperatures a thermometer reading from −10° to +100° and graduated in 0·1° was used. The bath was kept constant to ±0·02°.

When equilibrium was reached the undissolved acid was allowed to settle and the saturated solution was drawn through an asbestos filter into a weighing tube (Fig. 1). Above 55° the solution was blown over into the weighing tube to prevent vaporisation under the reduced pressure. The delivery tube was steam-jacketed to prevent crystallisation of the acid in the tube (Fig. 2).

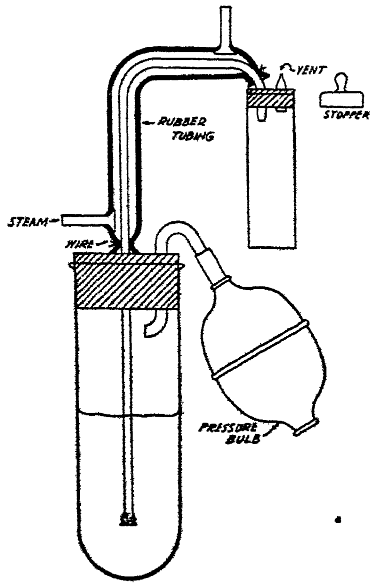



**Fig. 2.**

The weighing tubes containing the solutions were allowed ample time to come to room temperature before being weighed. The saturated solution was then carefully washed into beakers and titrated against standard sodium hydroxide solution, using phenolphthalein as an indicator.

The necessary time for the equilibrium was arrived at by taking samples every hour A number of determinations showed that six hours at least was required for equilibrium to be established between the solid and its solutions. The results in each case recorded below are the average of several obtained by approaching the equilibrium both from undersaturation and from supersaturation. Considerable difficulty was experienced in getting the sodium sulphate solutions to yield concordant results.

It will be noticed that the solubility of the phthalic acid decreases with increased concentration of the sodium sulphate. More marked divergence of the solubility is noticed between the 10 per cent and the 15 per cent salt solutions than between the water and the 10 per cent solutions. There is also great increase in solubility of the acid with rise in temperature. These facts can readily be seen by referring to Fig. 3.

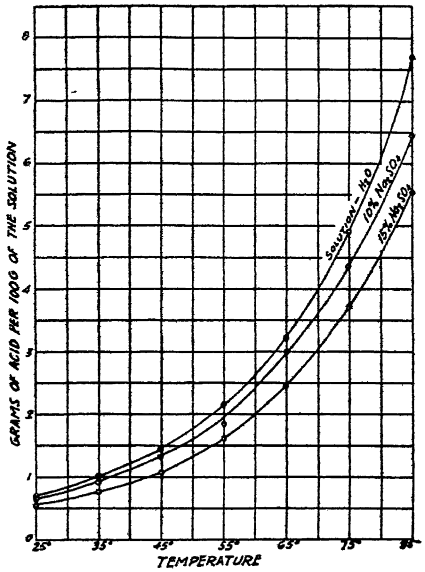



**Fig. 3.**

*Grms. of Phthalic Acid per* 100 *grms. of the Saturated Solution.*

| Temp. °C | Water | 10% $Na_2SO_4$ | 15% $Na_2SO_4$ |
|---|---|---|---|
| 25 | 0·7014 | 0·6440 | 0 5272 |
| 35 | 1·0125 | 0·9338 | 0·7575 |
| 45 | 1·446 | 1·341 | 1·080 |
| 55 | 2·168 | 1·858 | 1·630 |
| 65 | 3·246 | 3·018 | 2 455 |
| 75 | 4·926 | 4·373 | 3·748 |
| 85 | 7·687 | 6·461 | 5·533 |

—*Journal of the American Chemical Society*, vol xliii., No 5, May, 1921.

# NOTES.

"Infra-Red Spectra of Isotopes."—By F. W. Loomis.—*Separation of the Infra-red Absorption Doublets of HCl and HBr due to Isotopes; theory.* —If these bands are produced by the vibration of the nuclei along the line of centres of the molecules, the author shows that the frequencies should be approximately proportional to the square root of $(m_1+m_2)/m_1m_2$; hence the band lines due to $HCl^{35}$ and $HCl^{37}$ should differ by 1/1330, and those due to $HBr^{79}$ and $HBr^{81}$ should differ by 1/6478. In the case of the HCl band at 1·76$\mu$, Imes found doublets whose components agree in separation and relative intensity with the theoretical results. In other cases the computed separations are less than the resolving power so far used. — Abstract from the *Astrophysical Journal, November*, 1920, lii., 248-56.

The Excitation of Light by Cathode Rays in Air.—By Gordon S. Fulcher.—*Light Excited by Cathode Rays in Air.*—A beam of cathode rays, after passing through a hole in the anode of the

discharge tube in which the rays were produced, was placed at the focus of the collimating lens of a spectrograph, and the *intensity of the nitrogen bands* excited was determined for various discharge potentials and for various distances apart of the electrodes. The results show that, unlike canal rays, cathode rays in passing through nitrogen excite less light per collision the greater their energy, at least *for the range of speeds corresponding to from* 1500 *to* 3500 *volts.* Since the rays used were not homogeneous, the exact law of variation cannot be determined from the data obtained, but the results indicate that the light per collision varies inversely as a power of the speed somewhat less than the second; and it is pointed out that if, as is quite possible, the light intensity per collision varies with the speed in the same way as the chance of ionisation per collision, then the light intensity per ionising collision is independent of the speed.—Abstract from the *Astrophysical Journal,* December, 1920, lii., 278-85.

## BOOKS RECEIVED.

"The Popular Chemical Dictionary: A Compendious Encyclopædia." By C. T. Kinggett, F.I.C., F.C.S. Second Edition. Pp. viii+539. Illustrated. London: Ballure, Tindall & Cox. Price 21s. net.

"Atomic Theories." By F. H. Loring. Pp. vi.+218. London: Methuen & Co. Ltd.

"Confectioners' Raw Materials: Their Sources, Modes of Preparation, Chemical Composition, the Chief Impurities and Adulterations, their more important Uses, and other Points of Interest." By James Grant, J.P., M.Sc.Tech., F.I.C., F.C.S. Pp. 172. London: Edward Arnold & Co. Price 8s. 6d.

"Organic Analysis: Qualitative and Quantitative." By E. de Barry Barnett, B.Sc. (Lond.), F.I.C., and P. C. L. Thorne, M.A. (Cantab), A.I.C. Pp. xi.+168. Illustrated. London University Press. Price 7s. 6d.

## New Patents.

This List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W.C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

26571—Briggs, P. R.—Manufacture of sulphate of ammonia October 7.

26324—British Dye-stuffs Corporation, Ltd.—Manufacture of dyestuffs of the triarylmethane series. October 5.

26555—Forwood, G. F.—Treatment of hydrocarbons October 7.

26247—Imray, O. Y.—Manufacture of optically-active aromatic amino alcohols. October 4.

26214—Levin, I. H.—Electrolytic cells for generating oxygen and hydrogen. October 4.

26681—Wulfing, J. A.—Water-soluble compounds of diethylbarbituric acid and its homologues, and manufacture of same. October 8.

*Specifications published this Week.*

146234—Kolshorn, E.—Process for the manufacture of salts of compounds of lactic acid with tannic or gallic acids.

169513—Pratt, W. B.—Sulphur terpene compounds

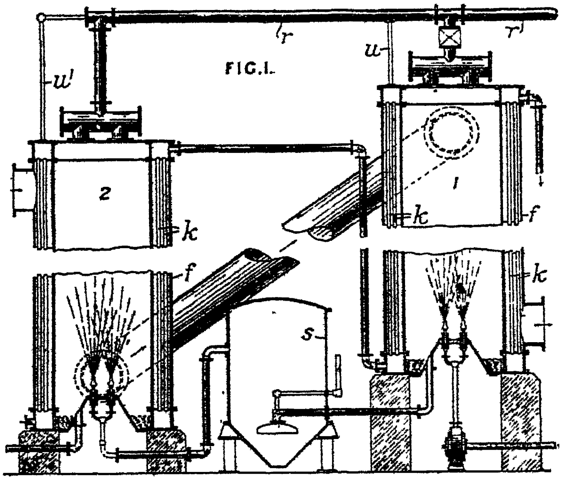
147711—Verien Chemischer Fabriken—Manufacture of hydro-fluoric acid from natural fluorides

169539—Dempster, Ltd, R & J., Knight, H. S, and Siddall, F. J—Combined generating and heating plant adapted to the manufacture of hydrogen.

169536—British Cellulose and Manufacturing Co. Ltd., Badder, W, and Nightingale, D A.—Manufacture of alkyl amines.

*Abstract Published this Week.*

*Distilling Ammoniacal Liquor.*—Patent No. 167719.—Messrs. Holmes & Co. Ltd., of Whitehouse Ironworks, Huddersfield, and Wyld, W., of West View, The Avenue, Roundhay, Leeds, have patented an improved process of distilling ammoniacal liquor, a suitable apparatus for which is illustrated in the accompanying drawing. The heated liquor is sprayed in succession into two or




more evaporating chambers 1, 2, the pressure in the first chamber being utilized to effect the spraying into the second. The liquor may be passed through an intermediate chamber *s*, in which it is mixed with a reagent to liberate fixed ammonia. The chambers 1, 2, are heated by flue gases circulating in jackets, *f*. The ammoniacal liquor is preheated by passage through tubes, *k*, in the jackets. Connecting pipes *u*, $u^1$, serve to pass the gases generated during the heating of the liquor in the tubes, *k*, to the collecting main, *r*, which leads to a saturator for the formation of ammonium sulphate. If pure ammonia is to be separated, the first evaporating chamber is surmounted by a column up which the vapours pass, and down which a portion of cold ammoniacal liquor flows and removes ammonia from the vapours. The liquor falls through the perforated top of the spraying chamber. The liquor from the base of the chamber is passed through a vessel, *s*, and then in succession through spraying chambers from which ammonia gas is withdrawn.

*Copper, Nickel, Sodium Salts.*—Patent No. 168097.—Mr. E. E. Naef, of 16, Loughborough Road, West Bridgford, Nottingham. has patented a new process of treating finely divided copper-nickel matte. A mixture of copper and nickel sulphides is heated with powdered caustic soda or with a mixture of caustic soda and sodium carbonate, common salt, sodium sulphide, sodium sulphate, or lime, and with or without the addition of a small proportion of powdered coal. The operation may be performed in an open or closed vessel, or in a rarefied or inert atmosphere, or in hydrogen. Sulphides, hydrosulphides and thiosulphates of sodium are formed and metallic copper and nickel are precipitated. Lime, with or without the addition of other salts, may be used instead of caustic soda, the temperature required being higher than in the case of caustic soda. The molten salts may be poured off, or the whole mass may be treated with water to dissolve the salts. The mixture of metals, may be separated by a carbonyl process, or it may be treated with sulphuric acic for the formation of nickel sulphate, the undissolved copper being refined electrolytically or converted into oxide and thence into sulphate.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

## NEW COMPANIES.

The under-mentioned particulars of New Companies recently registered are taken from the Daily Register compiled by Jordan & Sons, Limited, Company Registration Agents, Chancery Lane, W.C.2.

Amisol, Limited.—(177209)—Registered October 11th, 1921. To carry on the business of Manufacturing Chemists, Druggists, Drysalters, etc. Nominal Capital: £2,000 in 2,000 Shares of £1 each. Directors: To be appointed by Subscribers. Qualification of Directors. £100. Remuneration of Directors: To be voted by Company in General Meeting. Subscribers: T. Thomas, 1, Woodthorpe Terrace, Huddersfield, S. Wilman, "Norfolk Villa," Dewsbury; W. Sowden, "Fernleigh," 48, High Street, Cleckheaton; T. C. Hammond, "Hopewell," Lightcliffe, E. V. Chambers, "The Manse," Lightcliffe.

Brunt Chemical Co. Limited.—(177274)—Registered October 14th, 1921. 21, Cannon Street, Manchester. To carry on the business of Chemists, Druggists, Drysalters, Oil and Colourmen. Nominal Capital: £1,000 in 1,000 Shares of £1 each. Directors. Harry Herbert Brunt, "Aysgarth," Ashton-on-Mersey, (Governing Director), Herbert Brunt, 56, Longton Grove, Sydenham, S.E. Qualification of Directors: £100 Remuneration of Directors: To be voted by Company. Governing Director. £500.

## MEETINGS FOR THE WEEK.

*Tuesday, November 1.*

Mineralogical Society, at 5.30.—Anniversary Meeting. "On the determination of the optic axes of a crystal from extinction-angles" by Prof H. Hilton. "An example of quartz twinned on the Sardinian law" by Dr. J. Drugman. "Biographical notices of mineralogists recently deceased; with an index of those previously published in the Mineralogical Magazine" by Dr. L. J. Spencer.

*Wednesday, November 2.*

Society of Public Analysts, 8. "An Improved Specific Gravity Apparatus" by C. Butler Savory, M.D., M.Ch. "The Testing of Foodstuffs for Vitamins" by J. C. Drummond, D.Sc, F.I.C. and A. F. Watson, D Sc., A.I.C. "The Inks of Ancient and Modern Egypt" by A. Lucus, O.B.E., F.I.C.

*Thursday, November 3.*

Royal Society. "Spectra of Lead Isotopes" by Prof. T. R. Merton. "Experiments with Rotating Fluids" by G I. Taylor. "The two-dimensional slow Motion of Viscous Fluids" by Prof. L. Bairstow, Miss B. M. Cave and Miss E. D. Lang. "The Production of Single Crystals of Aluminium and their Tensile Properties" by Prof. H. C. Carpenter and Constance Elan. "On the Transmission Colours of Sulphur Suspensions" by Prof C. V Raman and B. Ray. "The Law of Distribution of Particles in Colloidal Solution" by Prof. E. F. Burton and Miss E. Bishop.

## NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemica Apparatus, &c., for review or notice to be addressed to the Editor.

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THE CHEMICAL NEWS.
VOL. CXXIII., No. 3212.

## CHEMICAL REACTIONS ON SURFACES.*

By IRVING LANGMUIR.

(Concluded from p 230)

IF $\theta_1$ is the fraction of the surface covered by this atomic hydrogen, then the chance that any given elementary space on the surface shall contain a hydrogen atom is $\theta_1$. The hydrogen atoms have a very strong field of force, since they are unsaturated chemically (for the electrons are not arranged in duplets). These atoms, therefore, have a relatively low rate of evaporation from the surface. Two atoms in adjacent spaces on the surface, however, may react with one another to form a hydrogen molecule. This is chemically saturated, and has therefore a weak field of force, so that it evaporates rapidly from the surface. The rate of evaporation of molecular hydrogen is thus proportional to its rate of formation from the atomic hydrogen, and this, in turn, is proportional to $\theta_1^2$ for the chance that *two* atoms shall lie in adjacent spaces is proportional to the square of the chance that an atom shall be in any given space. This statement of the problem lends itself readily to mathematical treatment, and the equations that were obtained for the dependence of the reaction velocity on the temperature and pressure are in full accord with experimental facts over a temperature range from 1500° K. to 3500° K. and pressures from 10 bars up to atmospheric pressure.

It is probable that the decomposition of ammonia, and also the formation of ammonia in contact with solid catalysts, depends upon similar interaction between adjacent adsorbed atoms. Reactions of this sort should be extremely sensitive to the actual distances between, and the arrangement of the atoms in the surface of the catalyst. If these atoms are a little too far apart, or if their electrons are not sufficiently mobile to permit of the electron rearrangement involved in surface reactions, the reaction will be much retarded. It is the opinion of the writer that these differences in the geometrical arrangement of the surface of the atoms is responsible for the "activation" of catalysts which is brought about by the action that takes place upon them. For example, if a plane surface of platinum be heated for the first time in a mixture of hydrogen and oxygen, the temperature has to be raised quite high before the reaction begins. When the reaction has occurred, however, even in gases at very low pressures, so that no appreciable heating effect takes place, the catalyst becomes modified and the reaction then proceeds, even at room temperature. In many cases, such effects are due to catalytic poisons, but there is good evidence that the effect is frequently caused by changes in the structure of the surface itself, brought about by the reaction. This is particularly noticeable in the catalytic oxidation of ammonia in contact with platinum wire After the wire has been used, the surface becomes very rough, and gradually a disintegration of the wire occurs, because of the surface changes taking place. The catalytic activity of the wire is very low when first used, but becomes much greater after it has become activated by the reaction itself.

The changes that occur in the surface of the platinum under these conditions seem to be exactly similar to those that are caused by rapid fluctuation of temperature. When tantalum filaments, or certain improperly made tungsten filaments, are run in lamps on alternating current, the wire shows a tendency to "offset," but this effect is entirely absent if the wire is heated to the same temperature by continuous current. This offsetting consists of a slipping of the crystals of the metal along the boundary planes. In extreme cases it leads to a nearly complete disintegration of the structure of the metal. Experiments show that this effect is directly dependent upon the rapidity of temperature fluctuation. Anything that increases the rapidity of temperature fluctuation, such as the introduction of hydrogen into the bulb, increases the rate at which offsetting occurs, so that it is possible in a few minutes to produce as much offsetting as would otherwise occur during hundreds of hours. Under these extreme conditions, the rate of cooling of the filament is of the order of a million degrees per second.

If a Coolidge X-ray tube is operated exclusively with direct current, even during manufacture, the surface of the target retains its high polish, even after long use. A few minutes' running with alternating current roughens the surface of the target, and it is well known that the focal spot in the target assumes an appearance which is quite analogous to that of the platinum surface used as a catalyst for the oxidation of ammonia. It is highly probable that the cause is the same in both cases, namely, sudden fluctuations in temperature between adjacent atoms in the material.

In a surface of crystalline platinum, where the atoms are presumably arranged in a definite surface lattice, the distances between adsorbed atoms which occupy adjacent spaces is probably a nearly fixed quantity, and in general it is unlikely that this fortuitous spacing is the best adapted to the interaction between the adsorbed molecules. When the surface atoms have been pushed around and made to assume new positions, arranged more or less at random, the distances between adjacent adsorbed molecules vary over a wide range, and some of these distances will be exactly right for the reaction to occur at the highest possible speed. The surface thus becomes composite, and there is then a relatively small fraction of the surface at which the reaction occurs with extreme rapidity, while over the larger part of the surface it takes place at a very slow rate.

When a surface has become so roughened that it is porous, the effective surface area increases, and the number of favourable locations for the reaction to occur may become much greater.

There is good evidence, however, that the activation is not merely due to an increase in the surface, for a surface which becomes activated for one reaction may not become activated for another reaction. For example, a plane surface of platinum, by a single treatment in a hydrogen oxygen mixture at low pressure, can have its activity so much increased that the temperature at which the reaction begins is lowered from 150° C.

* A Paper read before the Faraday Society

to room temperature, but this increase in activity for the hydrogen oxygen reaction is not accompanied by any change in the reaction velocity observed in the reaction between the carbon monoxide and oxygen.

The experimental evidence seems to indicate that the reaction that occurs between oxygen and hydrogen on the platinum results from interaction between adjacent adsorbed atoms, while the reaction between carbon monoxide and oxygen takes place between oxygen atoms adsorbed on the surface and carbon monoxide molecules from the gas phase which strike them. This difference in mechanism probably accounts for the different sensitiveness to surface conditions. It would also suggest that the energy imparted to the individual platinum atoms as a result of the reaction may be much less in the carbon monoxide reaction than in the hydrogen reaction. If this is so, the monoxide reaction should produce little change in the surface, and thus should not activate the catalyst for the hydrogen reaction.

The experimental evidence with carbon monoxide and oxygen on platinum (described in detail in another paper presented at this meeting), proves that nearly, but not quite all of the reaction between these gases occurs during collision of carbon monoxide molecules with the oxygen covered surface. In reactions of this kind, which occur as the result of collisions, we may expect that in some cases the exposure of the "flanks" of an adsorbed film to attack by colliding molecules may render them much more susceptible to chemical action. For example, it is conceivable—although in this particular case there is no experimental evidence for it—that, if the whole surface of platinum were covered by oxygen atoms, incident carbon monoxide molecules should be unable to react, while if only a certain limited portion of the surface were covered with oxygen, the monoxide molecules striking the oxygen atoms close to the place where they are attached to the platinum, might be able to react. In this case the oxygen film would be removed progressively from its bounding edge inward. It seems quite possible that this kind of action may be involved in some of the passivity phenomena observed with iron in electrochemical action, and may be also effective in causing the *sudden* beginning of the dissociation of hydrogen by a tungsten filament after small traces of oxygen have been consumed by the filament.

If we consider catalytic surface reactions with more or less complicated organic molecules, we should naturally expect that the orientation of the molecules and steric hindrance effects should become more important as factors in the mechanism of the reaction. For example, when ethyl acetate is heated with different solid catalysts, it may give—

A. $CH_3CO_2H+C_2H_4$
B. $CH_3CH_2CH_3+CO_2$
C. $CH_3COCH_3+CO_2+C_2H_5OH+C_2H_4$.

In all these cases, the —COO— group is unquestionably directly attached to the surface, while the rest of the hydrocarbon chain is located above this group. It is probable that the —COO— group is attached to the surface by primary valences, so that the bonds between these atoms disappear when the substance is adsorbed. Depending upon the different manners in which interaction between atoms and evaporation may occur, the resulting products differ. Reaction A involves only a shift in the position of a hydrogen nucleus, to allow the products to evaporate separately. In reaction B it is only necessary for a few electrons to shift their positions. Reaction C involves interaction between two molecules which must be adsorbed in adjacent positions in definite geometrical relations to one another.

*Reactions at Boundaries of Phases.*—Faraday observed that a perfect crystal of sodium carbonat eor sodium sulphate ("Experimental Researches," Everyman's Library Edition, p. 109) refuses to effloresce until the surface is scratched or broken, and that the efflorescence then spreads from the injured place Similar phenomena have been observed with copper sulphate and other crystals. In all such cases it is necessary to assume that the reaction (dehydration) *takes place only at the boundary between two phases.* Careful analysis (Langmuir, *Jour. Amer. Chem. Soc.*, 1916, xxxviii., 2263-2267) shows that wherever we have to deal, according to the Phase Rule, with separate phases of constant composition, the reaction occurs only at the boundaries of phases. Thus in the dissociation of calcium carbonate by heat, the carbon dioxide is produced only at the boundary between the calcium carbonate and the calcium oxide phases.

Dr. H. S. Taylor recently described experiments on the preparation of copper and copper oxide catalysts (Rochester Meeting, Amer. Chem Soc., April, 1921) in which he found that there was a long "period of induction" in the reduction of heated cupric oxide by hydrogen. All the phenomena that he observed in connection with this reaction are in accord with the view that this is another case in which the reaction occurs only at the junction between phases. In conventional nomenclature we may say that we have here an example of autocatalysis, the metallic copper accelerating the reaction. It seems much more profitable, however, to analyse the phenomena in terms of the probable mechanism.

The oxygen atoms in copper oxide are thoroughly saturated chemically, which means in this case that they have taken up two electrons from the copper atoms and have thus completed their octets, and leave the copper in the form of ions. Thus there is no reason for expecting a strong tendency to react with hydrogen at moderate temperatures. In view of Taylor's experiments, we conclude that the oxygen ions in cupric oxide are in fact very inert towards molecular hydrogen. Let us assume that, owing to some local imperfection in the space lattice of the atoms of the copper oxide, an ion of copper has taken up electrons and has formed a neutral atom. It is to be expected that such an atom should behave towards hydrogen molecules like metallic copper or other metallic substances. We have already seen that hydrogen molecules are adsorbed by platinum and by tungsten (and therefore probably by other metals) in the form of atoms. This action is presumably caused by the attraction of the "free" electrons of the metal upon the hydrogen nuclei. The hydrogen adsorbed by the copper in atomic condition can then react with the oxygen ions merely by the shifting of the hydrogen nuclei from the copper atoms to the oxygen ions, the electrons being transferred to another copper

atom Each hydrogen molecule thus supplies two electrons and is capable of converting and adjacent copper ion into a neutral atom. By such a mechanism it is clear that the reaction could proceed only at the junction between the phases.

## THE PREPARATION OF PURE PLATINUM.*

By EDWARD WICHERS.

THE Bureau of Standards has been working for some time on the preparation of the several platinum metals in a high degree of purity. In the course of the work on platinum in particular, some observations have been made which are of interest inasmuch as so-called pure platinum is in constant use in the collection of scientific data and in the control of industrial operations. Familiar applications are the use of the platinum resistance thermometer and the rare-metals thermocouple.

Since the chemical methods of detecting small quantities of impurities in platinum are not, in most cases, of proved reliability, it was decided to continue purification until the spark spectrum of the platinum should be as nearly as possible free from the lines of any foreign metal. It was found that repeated precipitation of ammonium chloroplatinate would yield metal of the desired purity. The platinum hereinafter described was obtained by four such precipitations, starting with material which contained significant amounts of palladium, rhodium, and iridium, as well as considerable iron, tin, and other base metals. These results are given because the impression has been more or less prevalent that pure or "thermo-element" platinum could not be prepared by this simple and economical method. The experience of Archibald (*Proc. Roy. Soc. Edinburgh*, 1909, xxix., 721), as well as others, in thus preparing platinum of any desired purity has not been sufficient to dispel the idea that some more complicated and tedious process is required.

Each precipitate of ammonium chloroplatinate was drained from the mother liquor in a Büchner funnel, then washed by stirring up the salt with a considerable volume of a 15 to 20 per cent solution of ammonium chloride, and again drained as before. This washing was always done twice, and sometimes three times. The washed precipitate was dried, ignited to platinum sponge in an electrically-heated muffle furnace, and redissolved by aqua regia. The solution was evaporated several times with hydrochloric acid in order to remove nitric acid, before the next precipitation. The amount of platinum left in the mother liquor from the precipitation was usually not in excess of 1 per cent of the platinum in the precipitate.

The final precipitate of ammonium chloroplatinate was ignited to sponge in a porcelain dish over a gas flame. The dish was covered with a silica plate and a stream of hydrogen run in to facilitate the decomposition, and incidentally to prevent the slight loss of platinum which accompanies the ignition of ammonium chloroplatinate in the air.

In addition to the spetrosopic tests, the thermoelectric method of comparison was used. (The e.m.f. developed at a hot junction between two dissimilar metals has long been made use of in the study of the platinum group. White (*Phys. Rev.*, 1906, xxiii., 449) employed the thermoelectric method to examine thermo-element wires for inhomogeneity and contamination during use. Burgess and Sale, and Burgess and Waltenberg (*Bur. Standards Sci. Papers* 254 and 280) applied the method to the study of the composition of platinum ware. Most alloys of platinum with other platinum metals or the base metals which are present as impurities give a positive e.m.f. against platinum itself. Thus an alloy of platinum with 1 per cent of rhodium gives about 2450 microvolts at 1200°, positive to platinum.) The least positive sample of Heraeus wire in the possession of the Bureau was used as a standard and will be designated in the subsequent paragraphs as "A."

The samples to be tested were prepared by melting the sponge on a piece of lime in the oxy-hydrogen flame The buttons were cleaned with hydrochloric acid and rolled into a thin strip with a small pair of flat rolls. There was apparently no perceptible contamination with iron in this process, although, as a precautionary measure, the strips were usually digested with hydrochloric acid.

The first samples prepared in this manner, although spectroscopically free from any trace of other platinum metals, invariably gave a considerable positive e.m.f. against "A." It was noted, however, that the spectrograms of these metals always showed the presence of calcium, and sometimes of magnesium.

Subsequent samples were prepared in the same way, except that the precaution was taken to use an oxy-hydrogen flame in which oxygen was in considerable excess, as suggested by Mr. Fairchild of this Bureau. Strips of platinum were then obtained wihch showed a *negative* e.m.f. against "A," varying from 2 to 38 microvolts at about 1200°. Upon direct comparison of several of our samples, together with "A," in the spark spectrum, the samples were found to be identical in all respects except for the presence of calcium and a trace of magnesium The variation in the intensity of the calcium lines was found to be roughly parallel to the variation in the e.m.f., the most negative sample showing only a very slight trace of calcium. This sample will be known as "K." A thermo-electric comparison was then made between "A" and three additional samples of Heraeus wire, as well as a sample of themo-element wire made by an American manufacturer. The last-named gave 10 microvolts, two of the Heraeus wires 40 microvolts, and the third 170 microvolts at 1200°, all positive to "A." The Heraeus samples were compared spectroscopically and again showed various amounts of calcium while the most positive one also showed the presence of rhodium. None of the specimens of platinum here mentioned had been used previously, and all were carefully cleaned to remove any superficial impurity before the spectroscopic examination.

Similar variations are shown by the several samples of Heraeus wire employed in the thermocouples used in the researches of Day and Sosman (*Carnegie Inst. Pub.*, 1911, 157) on the gas

* Published by permission of the Director of the Bureau of Standards from the *Journal of the American Chemical Society*, June, 192-

thermometer. The greatest difference is about 185 microvolts at 1500°. These wires were personally obtained by Dr Day from W. C. Heraeus, and were believed to represent the purest platinm obtainable.

Through the courtesy of Dr. Day, a comparison was made by Dr. W. P. White, of the Geophysical Laboratory, between the least positive of these samples (hereinafter designated as "B") and sample "A." "B" registered 18 microvolts. Later a direct comparison was made by us between "B" and our sample "K," the latter giving 21 microvolts negative at 1200°. On spectroscopic examination, the H and K calcium lines were found to be visible in K, and present with two or three times as great intensity in B. The magnesium line of wave length 2852·13 A° was faintly visible in both spectrograms.

From the fact that no differences were found in the spectrograms other than those mentioned with respect to calcium and magnesium, it is believed that a negative e.m.f. as obtained indicates higher purity and is not caused by the presence of some contaminating substance whose combination with platinum is negative to platinum itself.

It was also observed that the samples which contained the least calcium were remarkably soft, did not wet the lime as they were fused, and showed no perceptible recalescence on cooling Those samples which contained somewhat greater amounts of calcium were observed to wet the lime during fusion and showed a marked recalescence. A button which was properly melted but subjected to a momentary flash of a reducing flame immediately wetted the lime, showed recalescence on cooling, and gave an e.m.f. of 90 microvolts at 1200° positive to a duplicate sample, which was fused only in the oxidising flame. Strips of platinum containing appreciable amounts of calcium were found to show the characteristic calcium flame when brought to the melting point in an oxy-gas flame. Calcium was readily detected in "A" by this means.

The physical properties of the lime, and possibly its purity, seem to affect the purity of the platinum melted on it to a slight extent, but the pricipal factor is clearly the nature of the flame used. The data obtained seem to justify the conclusion that the calcium oxide undergoes some reduction if insufficient oxygen is used in the flame, and that the platinum takes up calcium and not calcium oxide. This was substantiated by melting nearly 200 grms. of platinm in an Ajax-Northrup induction furnace, using a tall porcelain crucible lined with powdered calcium oxide tamped around a mandrel. Under these conditions there is no possible source of reduction of the lime unless it should be by the platinum itself. The ingot which was obtained gave 5 microvolts negative to a satifactory sample prepared from the same sponge by melting in the oxy-hydrogen flame.

A few experiments were conducted to determine the suitability of crucibles made from magnesium oxide with a small amount of magnesium fluoride as a binder. A sample of platinum was melted in such a crucible surrounded by a graphite shell to act as a conducting crucible in an Ajax-Northrup induction furnace. The platinum was held at a temperature considerably above the melting point for about 15 minutes. The resulting button was extremely hard and brittle, and analysis showed a magnesium content of 3·0 per cent. A piece of foil similarly melted but held at about 1800° for three or four minutes showed a gain in weight equivalent to 0·33 per cent magnesium, assuming loss of platinum by volatilisation in this period to be neglible. This button was hard but could be rolled cold, and the resulting strip gave about 3000 microvolts positive to standard platinum at 1200°. Heating for several hours in the air caused the platinum to be coated with a greyish film, which was removed by borax applied to the strips during the heating. The e.m.f. was now considerably lower, indicating that a portion of the magnesium had been lost. As it was thought that the contamination of the platinum with magnesium might be due to the reduction of the oxide by the graphite, another sample of platinum was melted in such a crucible, but with substitution of a tungsten shell for the graphite. The resulting platinum button was again very hard and could not be rolled, and evidently contained considerable magnesium. A sample melted in a magnesia crucible in which no magnesium fluoride was used was also very hard. Although the tungsten could have caused a reduction of the magnesia, it is probable that the real explanation lies in the dissociation of magnesium oxide, whcih Tiede and Birnbraüer (*Z. anorg. Chem.*, 1914, lxxxvii., 129) observed as taking place rapidly at 1900°. A button of platinum melted on a cupel moulded from powdered magnesium oxide without a binder, by means of the oxy-hydrogen flame, was very soft, and registered 14 microvolts negative at 1200° to the Bureau's standard Heraeus wire. Under these conditions the magnesia evidently does not reach the temperature required for dissociation.

A passing reference to the alloying of platinum and calcium is made by Moissan (*Bull. soc. chim.*, [3], 1902, xxvii., 665), who observed that platinum, heated to boiling in the presence of lime by means of the electric arc, contained 2·54 to 3·01 per cent calcium. Tarugi (*Gazz. chim. ital.*, 1899, xxix., 1, 512) states that he obtained a platinum alloy with calcium by means of the reaction between a platinum salt and calcium carbide. Hodgkinson, Waring, and Desborough (CHEMICAL NEWS, 1899, lxxx, 185) obtained an alloy of the approximate composition $PtMg_2$ by passing magnesium vapours over platinum foil. In this connection the observation made some years ago by H. C. P. Weber ("Report of Committee on Quality of Platinum Laboratory Utensils," *J. Ind. Eng. Chem.*, 1911, iii., 688), of this Bureau is recalled. He found that certain pieces of platinum ware were alkaline to litmus after strong ignition. In one case at least Hillebrand obtained a definite qualitative test for calcium from the surface of an ignited crucible, and the inference was made that the calcium originated in the lime crucibles used for melting platinum, or in the lime salts used for polishing the finished ware. It is to be noted that while the present work indicates the presence of calcium as metal in the platinum, it would also be quite possible for ingots of platinum to enclose mechanically particles of calcium oxide, which might appear in the finished ware. It is clear from this that under favourable conditions the amount of cal-

cium taken up by platinum may be very significant, the more so when it is considered that the calcium will be gradually brought to the surface and removed and the properties of the platinum will therefore not remain constant

It has been mentioned that the purest samples of platinum thus far prepared still show the presence of calcium spectroscopically. The calcium content of this platinum is undoubtedly very small, the intensity of the H and K lines in Sample "K" indicating an amount which is probably not in excess of 0·0001 per cent. An attempt will be made not only to determine the amount of calcium as definitely as possible, but also to approach still more closely the goal of absolute purity. It is proposed to make a study of the suitability of other refractories, such as thoria and zirconia, for melting pure platinum, and also to determine the optimum conditions for melting platinum on lime, inasmuch as this substance commends itself so highly because of its cheapness and availability.

It is further planned to make use of the temperature coefficient of resistance as an index of the purity of the various samples. This would furnish an experimentally determined quantity peculiar to the material examined and independent of any arbitrary standard of comparison such as must be used in the thermo-electric method. Such determinations would be of great value in the subsequent standardisation of new material. This method has the added advantage that the values obtained are capable of variation in one direction only, so far as is known, while the e.m.f. of a given sample may be positive or negative to absolutely pure platinum, depending upon the nature of the impurity.

Acknowledgments are made to Mr. F. W. Smither, under whose supervision the chemical work on platinum is conducted, and to the other members of the Bureau staff who assisted in this work, in particular Dr. W. F. Meggers, Mr. C. O. Fairchild, and Mr. Louis Jordan.

## TRAINING FOR FOREIGN EXPLORATION.*

By H. FOSTER BAIN,
Director United States Bureau of Mines.

MINING engineering occupies a borderland. In common with other branches of engineering it is an "art and science by which the mechanical properties of matter are made useful to man in structures and machines"—but with a difference. The civil engineer digs a hole to put something in it, a foundation perhaps. The mining engineer digs a hole to get something out of it, the ore. If he puts anything into the hole, timbers to support the excavation perhaps, he does it grudgingly, and always with a view to the utmost economy of material. He cannot, as can his fellow professional, build with an eye to the long future. He must always face the fact that his main object is to get things out of holes, and that when he has got out of a hole all that nature had put in it, neither the hole nor the plant used in the work has any further value. There is but a modicum of salvage upon which he may count. In many particulars his work shows analogies to that of a contractor, and the same logic that leads a contractor to low first-cost installations is good within reason, for the mining engineer. He does his work and moves on, and there is probably no profession calling for equal skill and learning in which the members wander more. Always they are seeking or extracting or utilising materials forming part of the crust of the earth, and usually are doing it under conditions or with equipment that is at least suggestive of being temporary. The mining engineer must improvise, and he must be versatile. Of him it may be written as Kipling has of the marine:

> "For there isn't a job on the top o' the earth the
> beggar don't know nor do,
> You can leave 'im at night on a bald man's 'ead
> to paddle 'is own canoe.
> 'E's a sort of a blooming cosmopolouse—soldier
> and sailor too."

To the lore of the geologist he adds the skill of the engineer and the science of the metallurgist. Always and everywhere an eclectic he adapts means to the end. Clearly where there are such varied duties and opportunities room for specialisation exists, and this is, indeed, the fact.

Mining engineers, employing that term in the broad general sense in which it has common usage, are called upon for three sorts of work: (*a*) geological; (*b*) mining proper; and (*c*) metallurgical. No one man may be expected to be competent in all three, and each branch is really a profession within a profession, but a man who stays long and achieves success in mining engineering must know something of all three, and young men who leave the schools, regardless of the point of the triangle at which they begin, seem in practice liable to end at either of the other. Each of the three has applications outside mining or verges over into other fields. Thus the border line between metallurgy and chemical industry is shadowy, the ties between mining engineering proper and civil engineering are many and close, and geology is a broad science which touches many fields aside from those related to ores and minable minerals. It is, however, the light that geology throws on the genesis and especially the occurrence of ores and minerals that interests the miner, and it is in finding minerals and guiding development that it is of most direct benefit to him. This work is fundamental to mining And it is the work of the exploration engineer. It may be of interest to inquire as to the probable future demand for his services and the training necessary to qualify him for service. Since mines are wasting assets, the very life of the mining industry is dependent upon the continual finding of new mines, new ore bodies, and new reserves. When this stops, mining will stop, though the death may be a lingering one. Whatever may be true as to a particular type of mining, or mining in a particular locality, it must further be clear that so long as man persists on this earth he will have use and need for some portions of its crust, and that, therefore, mining in some form will continue. Each individual mine, be it ever so long lived, is eventually worked out and becomes worthless, and other mines must be found to take its place. The emphasis changes and minerals or metals

* Forty-eighth Annual Commencement Address, delivered on April 29, 1921, and reprinted from the *Bulletin* of the School of Mines and Metallurgy, University of Missouri, June, 1921, No. 3, vol. xiii.

eagerly sought by one people or one generation are less important to those who come later, sometimes because their wants are supplied from a different source. In the early settlement of the Mississippi Valley, local salt supplies were so important that salt lands were generally set aside as being of particular value. Now these local supplies are of so little importance that they are generally not worked. Nevertheless the salt industry is many-fold larger and more important than was contemplated by our grandfathers. The human need for salt is as great as ever, and with increasing population more salt, and hence more salt mines have been needed.

As there comes to be more people in the world there will be more need of mineral products, and disregarding the substitution of one for another, the minimum rate of increase in output for the minerals as a whole may be safely taken as that of increase of population.

There is an additional factor that lends assurance to the future of mining As civilisation spreads and industrialisation becomes increasingly intensive, the per capita consumption of minerals increases. Man comes more and more to depend upon energy taken from the earth to supplement his own labour. The brilliant civilisation of the Greeks was based upon slave labour. It is worth remembering that in the golden age, which the classicists so love to recall, the mines of Larium, worked by slaves, were so productive that each citizen of Athens received a dividend in place of an annual tax notice. Naturally they had time to sit around in the sunshine and talk philosophy. The people of our times will not tolerate slavery. We have found a better way in that we harness to our use the energy of falling water and of fuels and so are each served by invisible, non-consuming genie of the earth. The peoples who make the most use of earth materials and forces are the peoples who work the shortest number of hours, produce the most goods, and have the most to divide among themselves. There are great differences between the peoples of various countries and centuries in this particular. Probably the civilized man, on the average, eats little if any more food than his ancestors did, but he does burn more coal and uses more metals. Even among the various peoples of the present there are differences. The Chinese use about one-twentieth of a ton of coal per capita per annum. Americans use approximately six tons, and other peoples use various amounts between. Generally speaking, the world is learning to use more and more coal and so to substitute the mechanical energy of heat for human labour. The pre-war per capita consumption of copper in the United States was 6 to 7lb., and for France about ½lb. In Russia it is much less, but nothing can be more certain that that through a term of years the peoples of other countries are going to approximate more closely to American standards of consumption. The United States is by no means the only country where modern plumbing is appreciated, and as the cult of the bath-tub spreads around the world the consumption of the metals will grow. This demand can only be supplied by re-use of old metal or by making addition to the world's stock. Mineral wealth, fortunately, is not necessarily consumed in use. There is wastage, but there is also salvage, and large amounts of old metal are continually returning to use, so much so that important metallurgical processes, such as making open-hearth steel and cement copper are based upon supplies of scrap metal.

The existing stocks of the various metals represent accumulations of all the centuries that have gone before, though very much the larger part has been won within the last hundred years. There have been times in the past when but little was added to the stock, and there have been peoples who merely captured in war and used the metals mined by others. This was true of the Tartar dynasties in China. The peoples who ceased to mine ceased to progress in civilisation, and the great civilisations of the past were those in which the people laid under tribute more and more of the earth.

As yet no peoples are known who have accumulated a sufficient stock of metals to supply themselves by remelting, and at the same time to make progress in civilisation Having regard to the many activities that lead to wastage it seems improbable that any active people will reach the stage where they will not require periodic additions to their stock of metals. In the opinion of economists, also, no active people have yet reached a point of saturation as regards even steel, the most common of our metallic alloys. It seems, therefore, safe to assume that demand for minerals will continue to increase.

Two methods of meeting this increasing demand are known. By improvements in technology and financing it will be possible to lower the limit of metal content which separates ore from waste and so increase the reserves in known deposits or make into ore deposits what are now mere mineral segregations. This is a fruitful field and calls for application of the highest type of skill and genius in our profession. It is one in which remarkable results have been achieved. Working 1 per cent copper ores means handling 2000lb. of material to recover less than 20lb. of copper, for even the best practice involves losses. It is only possible to do this by application of excellent technology and remarkable powers of organisation and financing. In producing helium from natural gas a raw material containing less than 1 per cent is used, and the technology involves incursions into low temperatures and high pressures not previously applied on any large scale outside physical laboratories.

A second way to meet the future demand for mineral products is to discover new deposits either of types made profitable by the improvements of process and business organisation just mentioned, of types long known, or of new types. Fortunately there are opportunities of finding all three, and in all this work exploration enters. The search for "porphyry coppers" has been a wide one. Beginning in the United States, it has long since spread into foreign fields. It has led men into many of the odd corners of the earth, and there are regions yet to be explored. In conducting this work, knowledge of the widest character is desirable. When Mr. C. G. Gunther began his search in Mediterranean countries, which has resulted in the development of an American mine of promise on the Island of Cypress, the first step was a reading of the classics. The Romans and earlier rulers of the region had sources of copper

which, while small as judged by present American standards, might, it was thought, well point the way to a source for modern production. It will be recalled that the Utah, Chino, Ray, Nevada Consolidated, and other of our modern enterprises built on older small-scale undertakings. Mr. Seeley Mudd, the eminent mining engineer, who studied in a Missouri school and began his professional career in a Missouri copper mine, had the vision of applying in the Mediterranean region the knowledge which had grown out of American experience. He and his associates found in Mr. Gunther an excellent, enthusiastic agent. The work began, as I have intimated, with a careful review of the classics, and was followed by field studies first in North Africa and later in Asia Minor, where old mines offering promise of profit under modern methods were found. I cite this instance to enforce the observation that no knowledge comes amiss to an exploring engineer. I hope it will not be construed into an argument for making Greek and Latin required courses in mining schools, but it does show that wide learning is of real value to a mining man who proposes to do more than conduct a local and minor operation. As for Greek and Latin, mining men as well as others who can without undue sacrifice of time become acquainted with them will gain by doing so. It is well, though, to preserve a sense of proportion, and mere knowledge of foreign languages, ancient or modern, hardly qualifies one to assume responsibility as operator or advisor in mining. Indeed, a surprising amount of work can be done through interpreters, since to a good geologist the rocks speak direct, and a competent miner or metallurgist can piece together the story of old works and furnaces from scattered remains, drawing deductions as surely as does the vertebrate palæontologist from a few bones. Get all the knowledge of modern languages that circumstances permit. Some have a facility in this which carries them far, but remember that it is but a means to an end. In the course of a recent professional trip lasting some twenty months, business took me into countries and regions where eleven distinct languages or dialects were used, so distinct that for each interpreters were necessary. If I had stopped to learn each language before transacting business, I would never have found time to do the work for which I was sent. Such experiences are not unusual in these modern days of wide travel. It is helpful, but not necessary, to know modern languages Even when no interpreter is available, a few simple words will carry you surprisingly far. It is not only that they are useful in themselves, but they help to establish friendly relations. People generally take it as an effort to good understanding that you have tried to become qualified to talk to them in their own tongue, and words in any language carry an accumulation of associations which is left behind in translating. You must, however, depend largely on yourself. Use your eyes and your feet. Get out into the field and observe. Leave, if you must, puzzling questions as to labour supply, laws and regulations, until you can get a competent interpreter, but for the facts as to character and extent of the deposit you wish to see depend on your own powers and energy.

I am speaking now of language study as a means. Language and the whole group of so-called cultural studies have another use, one not to be overlooked. If you purpose to be an exploration engineer, you will spend much time away from home, often under uncongenial surroundings. I once asked a young man returning from an outpost in West Africa what he considered most important for one to have before going into such work. I was a bit surprised when he answered, "a college education." Experience had taught him that a well-stored mind is the best companion, not only in solitude, but of a man surrounded by primitive and brutalising conditions to which he does not wish to succumb. It has been my experience to note young men of good antecedents who have dissipated and become mere brutes when left alone among savage or nearly savage people for lack of mental reserves Mental balance and mental resources are of peculiar value as stabilisers under such conditions.

Search for "porphyry coppers" and similar deposits will almost certainly carry you into regions of ancient mining. It is well to be on your guard neither to underestimate or overestimate the older civilisations The ancient miners did many things well. They are apt to have exhausted the bonanzas down to the water level, and high-grade ore in old workings is rare. Their costs were low since the mines were operated mainly by slave labour. It does not follow that because others worked a mine for centuries, or even because it yielded considerable aggregate of metal, it can profitably be exploited under modern conditions. With primitive tools the ancients accomplished wonders. There is, however, one assumption that it is usually safe to make—they did not work far below permanent underground water-level, since no amount of human labour quite accomplishes the work of modern pumps.

Just as we must remember that price relations of labour and metal were in ancient times very different from those of to-day, so we should bear in mind that in the past people were satisfied with amounts of metal that would be considered insignificant now. Mr. E. C. Eckel has pointed out that at the time of the discovery of America, the total amount of gold accumulated in Europe in all forms was worth less than $100,000,000, and that up to the American Revolution the iron made annually in this country was but 15,000 to 25,000 tons Even at that it was equal to the output of England. Many deposits which would satisfy such demands are of no importance whatever under modern conditions of business and technology. Whole groups, therefore, of ancient workings may be passed in review quickly once you are satisfied as to their type and average extent.

Finding deposits suitable for large mining enterprises is, however, not the whole of the work of an exploring engineer. He may be employed to look up sources of some mineral which does not occur in large bodies, such as tungsten or vanadium. In such cases little bodies must be regarded as jealously as are large ones of cheaper metals. A due sense of proportion is of high value to him, and an intimate knowledge of the mode of occurrence of the mineral he is seeking to find is a first essential. Placer gold has a

natural habitat, and there are characteristic differences in types of deposits which may be correlated with the character of the country rocks, the extent of their metamorphism, the presence or absence of intrusives, the character of the latter, the physiographic history of the region and similar geological features. Much is known now of metallogenic provinces, and something of paleogeography. All this and more is useful to one engaged in finding ore.

In estimating the value of professional knowledge necessary for success as an exploring mining engineer, I would, therefore, place a good working knowledge of geology first. This should extend not only to the technic, but to the sources of information and to current knowledge of the geology of the region to be explored. A metallurgist or a mining engineer engaged in operation of properties does not need so comprehensive an understanding of geology. It is sufficient if he knows the general scope of the science and the particular ways it may be applied to problems he must face It is by no means necessary that he should be versed in its technic, since there will always be within reach men skilled in the art who may be called to his assistance. What he should know is when a geologist can be helpful and how to use him in his work. It would be better for such men to concentrate their time and energy upon acquiring a complete mastery of their own work rather than an amateur and probably misleading knowledge of geology.

In the case of the exploring engineer the case is different. His prime function is to find ores, and to do this he must know ore bodies and the laws which govern their occurrence. These laws are imperfectly understood,; much regarding them remains to be learned, and to resolve these doubts calls for the most complete knowledge obtainable concerning the principles of geology, the history of the earth, and the technic of making geological studies. It is therefore important that the exploring engineer should be first of all a well-trained geologist, one capable of observing, recording, weighing, and judging the numerous facts of which account must be taken in making his determinations.

Much observation has convinced me, though as to this there are differences of opinion, that it is better if he learn his geology first as a scientific study. There is a high value in the detached point of view of the man who loves science for its own sake and counts truth as most important. Men so trained have usually more vision. They have a wider knowledge of the literature of the subject and of the work of others. They are less eager to accumulate only the facts of immediate importance and so have more facts and more theory upon which to fall back when in difficulty. They do their work better because they look over the whole problem first. Not infrequently they make large savings by eliminating unprofitable work through preliminary study of literature. For all these reasons I would recommend the man who purposes to devote his time to exploration to study geology first and to study it as though he expected to be a professional geologist.

This, however, is not alone enough. It requires but little knowledge of the field to recognise that many serious mistakes have been made through relying on the advice of geologists. For this particular work of finding ore is needed more than the usual equipment of a good geologist The latter is rarely versed in economics, and this is almost equally essential. Too many geologists have no adequate understanding of the relative importance of things from the miner's point of view. Not being trained in assuming financial responsibility for mistakes, they are cheerfully optimistic when to be unduly so invites failure. Their first tendency is to general advice, and all too promptly they will sketch out plans for development that call for millions when perhaps thousands alone are available. The geologist, therefore, needs further training before he is properly prepared to advise regarding mining development. As a geologist he is what one may call semi-finished material, though, I would have you understand, most excellent material for further manufacture.

When the prospective exploring engineer has completed his scientific studies he needs help and criticism from his fellows, the mining engineer and the metallurgist. It is not necessary that he should become equally learned in their branches of the profession, but it is essential that he have a clear conception of the scope, character, and limitations of their work. It is his business to find the ore which the mining engineer shall mine and the metallurgist treat Clearly no one will be profited by his finding and mapping metalliferous segregations which cannot be mined or are not amenable to treatment. It may be highly interesting and of great scientific import to map such bodies of mineral, but that is the function among others of the geologists of official surveys. The exploration engineer must work to find something out of which a profit may be made or he has not found ore. Clearly he must know, at least in general terms, the limits of cost which separate ore from rock, and he must have some well-defined ideas of the technical difficulties to be overcome in mining each particular deposit, and of the methods likely to be applied. It is not necessary that he should be able to make the application. That calls for skill of another character, but he must know, and know surely, that some one of several methods, perhaps, may be applied, and must be able to approximate the cost. It is useless to find and drill placer ground where the boulders are too large and numerous, or the bottom too hard or pinnacled to permit dredging, while the supply of water, of storage space, or the grade prevents hydraulicking or sluicing. There are dry placers, it is true, but if the exploration engineer finds conditions so unfavourable he would do well to defer drilling until after taking expert advice as to methods and costs of dry washing It is also useless to spend money on a careful examination of a placer property unless there is reason to anticipate that the gravel will yield as much or more than the cost of working elsewhere under similar conditions. To determine this, one must know what constitutes similar conditions and what usual and unusual costs are. It is no part of the ordinary training of the geologist to accumulate such data, and if he is to succeed in exploration he must draw on the experience of the engineer for it, either by serving an apprenticeship under him, or having always a competent engineer as an associate. The latter is not always feasible, and

it is greatly to the benefit of his future if the geologist will serve for a time as helper to a good engineer in operating or examination work. It will help him to get into the habit of quantitative thinking, and he will learn much of the law of averages. For one thing, engineering methods of sampling are on a much sounder basis than are those of the geologist. It is one of the minor tragedies of scientific work that so much high thinking is done over non-representative samples. Geologists generally have the same naive confidence as has the prospector and promoter in their ability to take a "grab" sample which will be representative, and this is a common source of error and disappointment.

Having said so much in disparagement of the profession which I have long loved, let me add that in the study of placers there is no knowledge that entirely compensates for lack of clear conceptions of geologic history and skill in geologic interpretation. Placers are the products of rivers or beach action. Their accumulation is an incident in river, lake, or marine history, and may be closely correlated with the physiographic history of a region. There are definite places at which they may be expected to occur, and others at which it is useless to seek them. Frequently they relate back to ancient rivers and to physiographic stages in the past whose marks, obscured by later changes, may be picked up only by the skilled eye, and of which the evidence may be correlated only by an active, well-trained brain. To indicate the need of supplementary training and experience is not to discredit what is sound and useful in that already given to geologists. While I have drawn my illustration from the field of placer mining, a similar argument may be made in the case of lode mining, where structure, secondary enrichment, and other phases of geology are equally important, but where also it is necessary to know in outline of mining methods, especially of the critical limits, both technical and financial, of their application. The situation is the same in exploration for gas and oil except that petroleum technology, being newer, is not as yet well formulated, and the financial limits are more elastic. The rewards of success in oil and gas production are so much larger in proportion to the immediate investment, and the returns are so much more prompt, that it is not possible to estimate probable costs as closely as in other forms of mining.

Consideration of costs leads one into the larger field of economics, a popular branch of learning just at present. Aside, however, from this new general interest in what was once called "the dismal science," and belief in its applicability to present-day problems, there are permanent reasons for the exploring engineer acquiring more than a slight acquaintance with economics.

(To be continued).

## DICTIONARY OF APPLIED PHYSICS.

A "Dictionary of Applied Physics," an important work which Messrs. Macmillan have arranged to publish under the Editorship of Sir Richard Glazebrook, is now in an advanced stage of preparation.

The work, which is elaborately illustrated, will appear in five large octavo volumes, containing some 600 to 700 pages each, dealing respectively with :—

I. Mechanics—Engineering and Heat. II. Electricity. III. Metrology, Meteorology and Measuring Appliances. IV. Metallurgy and Aeronautics. V. Optics, Sound and Radiology.

The Editor has been fortunate in securing the assistance of a distinguished body of Contributors, and it is hoped that Vol. I. will be published in the early part of 1922. It will contain articles on Thermodynamics, the Theory of the Steam Engine, the Liquefaction of Gases and Refrigeration, by Sir Alfred Ewing. Sir Charles Parsons and Professor Stoney, with the assistance of their respective staffs, have written on the Steam Turbine; Sir Dugald Clerk and Mr. Burls on the Internal Combustion Engine; Professor Dalby on the Balancing of Engines; and Dr. E. H. Griffiths on the Mechanical Equivalent. The Editor is indebted to Dr. Horace Lamb for several articles on mathematical questions connected with the subject of the volume. Dr. Stanton has contributed an article on Friction, Mr. W. B. Hardy writes on Lubrication, and Mr. G. S. Baker on Ship Resistance. Mr. Jakeman, Mr. Batson, Mr. Hyde, and other members of the staff of the National Physical Laboratory have written on Manometers, the Determination of the Elastic Constants of Materials, Dynamometers and similar subjects. Mr. Southwell writes on the Theory of Elasticity, and Mr. Landon on the application of that theory to Structures. Professor Fulton treats of Hydraulics, and Professor Bulleid of the Kinematics of Machinery.

In the Heat Section, Messrs. Day and Sesman have discussed the Experimental Realisation of the Absolute Scale of Temperature; and Dr. Coblentz, of the U.S. Bureau of Standards, has contributed an important article on the Experimental Verification of the Laws of Radiation. Some account of Radiation Theory, with a short Article on the Quantum, is due to Mr. Charles Darwin; while Mr. Whetham has written on the Phase Rule. Articles on Calorimetry in its various branches and on Pyrometry have been contributed by Mr. Ezer Griffiths; Professor Porter has written on Thermal Expansion; Mr. Schofield on the Conduction and Convection of Heat; and Mr. Higgins on Thermometry, Viscometry and Flash Point Determination.

From the above particulars it will be seen that success has attended the Editor's efforts to secure, in each important subject, an Article from a recognised authority, and this same plan has been followed with equal success in the other volumes, which will appear at short intervals after the first.

## PROCEEDINGS OF SOCIETIES.

### SOCIETY OF GLASS TECHNOLOGY.

THE opening meeting of the Session 1921-22 was held in the Applied Science Department, The University, Sheffield, on Wednesday, October 19, 1921, the President, Dr. M. W. Travers, F.R.S.,

in the Chair. The following papers were read and discussed:—

"*The Comparative Compositions of Pot Clays from the Stourbridge District during the last* 50 *years.*" By G. V. EVERS.

"*The Properties of Lime-Magnesia (Dolomite-Lime) Glasses and their Commercial Application.*" By VIOLET DIMBLEBY, B.Sc., S. ENGLISH, M Sc. F. W. HODKIN, B.Sc., and Prof. W. E S. TURNER.

## NOTES.

BRITISH DEVELOPMENTS IN NITROGEN FIXATION.—The synthetic ammonia factory at Billingham, designed to manufacture about 60,000 tons of ammonium nitrate annually for war purposes, was commenced by the Ministry of Munitions early in 1918, but at the time of the Armistice was only very little advanced. It has since been taken over from the Government by Messrs. Brunner, Mond, & Co. Ltd., and is being re-designed to manufacture peace products, chiefly fertilisers. The subsidiary company they have promoted, Synthetic Ammonia & Nitrates, Ltd., will have a capital of £5,000,000, is at present concentrating upon designs for an initial plant to produce 25 tons of ammonia per day, or about 6,000 to 7,000 tons of nitrogen annually. Their works are, however, being laid out so that this small nucleus installation may be quickly enlarged to 100 tons per day, and afterwards to a maximum capacity of 300 tons per day, or about 80,000 tons of nitrogen annually. The original Government site of 260 acres is being increased to about 1000 acres in all, and two ship berths on the River Tees have been acquired. This increased accommodation has been found necessary in order to give ample room for the development of the whole scheme, which includes the manufacture of a number of by-products. There is also to be an oxidation plant of a capacity of 10,000 to 12,000 tons of nitric acid annually. A British company, Cumberland Coal Power & Chemicals, Ltd., has also been formed to erect works in England to operate the Claude process for the manufacture of synthetic ammonia. Information to hand states that a full-size commercial ammonia unit, working at 1000 atmospheres, is now running satisfactorily in France, producing at the rate of 5 tons of ammonia per day. The British Cyanides Company are continuing at Birmingham their large-scale experiments on fixation of nitrogen by the barium process, employing fuel-heated furnaces. Though these experiments have been partially successful, final conclusions as to the ultimate possibilities of the process have not yet been reached. The works works erected at Dagenham by the Nitrogen Products Company to manufacture ammonium nitrate during the war period from cyanamide by the Ostwald process are now closed.—From the "Report of the Nitrogen Products Committee, Ministry of Munitions."

THE VACUUM HOT-SPARK SPECTRUM OF ZINC IN THE EXTREME ULTRA-VIOLET REGION.—By R. A. Sawyer.—*Hot-Spark Vacuum Spectrograph for Extreme Ultra-Violet.*—After reviewing briefly the work of Schumann and Lyman, the author des ribes the apparatus by which spectra extending to less than 300 A were obtained. As source of light, a condensed spark was used which, it has been found, can be passed between electrodes a millimetre or less apart if sufficiently high potentials are applied, even in extreme vacuum. This source and a specially ruled, short focus, concave grating and the slit and the plate-holder, each provided with the necessary adjustments, were mounted inside a brass tube, a meter long by 15 cm. in diameter, which was kept evacuated by a diffusion pump. On account of the gas given off by the electrodes, a series of sparks lasting 5 seconds could be allowed only every 5 minutes or so, but 20 to 30 minutes' total exposure was sufficient as a rule. After precautions were taken to minimize the corrosion of the grating by active gases and also fogging due to stray light and gaseous discharge, highly satisfactory results were obtained. *Ultra-Violet Spectrum of Zinc, 2200 to 316 A*.—The wave-lengths of about 100 new lines probably due to zinc, 80 of which are below 1400 A, are given in Table I., accurate to about 0·5 A. See Plate X for spectrogram.—Abstract from the *Astrophysical Journal,* December, 1920, lii., 286-300.

THE CHEMICAL INDUSTRY IN HUNGARY.—The report upon the Hungarian chemical industry, read at a meeting of the National Society of Hungarian Chemical Products' Manufacturers, states that of the 245 works formerly in Hungary, there are now only 175, but there are hopes that before long new productive branches will be found. Those requiring large quantities of raw materials have little chance of great development for the moment, but manufacture of demi-products is promising. In spite of almost insurmountable obstacles, the Hungarian works during the last few months have not only met home demands, but also produced material for exportation, valued at several hundred of millions of francs, and everything indicates that Hungary will play a prominent part in the south-east of Europe, as soon as the restrictions now existing are abolished. The entire chemical industry is reviving, although Hungary has lost her salt works and those for manufacturing explosives, paper, and ethers. On the contrary, the manufacture of pharmaceutic and organic products is very flourishing. In the event of a good harvest, the alcohol, bone, fertiliser, starch, oil, and margarine industries will revive. Manufacture of soap, candles, colours, varnish, artificial silk and rubber is satisfactory.—*Industrie Chimique,* September, 1921.

MR. EDMUND WHITE, B.Sc., F I.C., ex-President of the Pharmaceutical Society of Great Britain, delivered the inaugural address when the Welsh College of Pharmacy was opened at Cardiff on Wednesday, and the medals and prizes for last year's work were presented to the successful students. Mr. White said that he had inspected the new College, and was very pleased with what he had seen. Cardiff was certainly among the first technical colleges to carry out the pharmaceutical training of students, and their school was one of the best. Principal Coles, reporting on the work of the department in the last session, said 15 students passed the Pharmaceutical Society's examinations and were now fully qualified chemists; nine of the previous year's students

had also passed. For the present session they had 55 full-time students, including 21 ex-service men, as compared with 22 last year. This showed that the school was becoming better known, and, as far as he knew, it was one of the biggest departments of its kind in the country. Out of the 15 students who passed the full test last session three were ladies.

ZINC CONCENTRATES.—The Board of Trade announce that they have instructed their agents in Australia to ship a supply of Broken Hill zinc concentrates to this country, and will be prepared if desired to maintain supplies to meet the immediate requirements of smelters in the United Kingdom. In order to enable smelters to re-start their works and provide employment, the Board will be prepared to consider offers for these concentrates delivered at works Offers for future deliveries over a period will also receive consideration. The British Metal Corporation, Ltd., of 3, Abchurch Yard, London, E.C.4, have been appointed the agents of the Board of Trade for all business relating to concentrates for disposal in the United Kingdom, and all enquiries as to prices, terms, &c., should be addressed to the Corporation.

THE Sixth Annual Report on the work of the prescription pricing department of the Cardiff Insurance Committee, which prices chemists' prescriptions for the insurance committees in Wales and Monmouthshire, and for the Welsh National Memorial Association and the Pembrokeshire County Council, shows that the number priced in 1920 was 1,670,184, representing an increase of 31,562 on the previous year. The average number of prescriptions per insured person was approximately the same as for the year 1916, but the average prescription cost per person increased from 1s. 6·37d. in 1916 to 2s. 8·53d. in 1920 Increased ingredients cost and higher dispensing fees are responsible for the average cost per prescription being 4½d. more. The net expenditure of the pricing department for the year was £2,243.

PLATINUM metals may be detected by the "glow reaction" of Curtman and Rothberg as used by Logan ("Platinum and Allied Metals in California: Cal. State Min. Bur., *Bulletin* 85, 1919, p. 102). The test depends on the catalytic effect of finely divided platinum metal in the oxidation of illuminating gas. The material to be examined is dissolved in aqua regia and the test applied without any previous separation of elements The test is more sensitive if the solution is not too acid. A very thin piece of asbestos paper, held by one end with tongs, is alternately dipped into the solution to be tested and heated until about 0·2 cubic cm. has been absorbed. The asbestos is then heated to redness, cooled until the redness is no longer visible, and then thrust at once, while still hot, into a stream of mixed gas and air from a Bunsen burner which is regulated to deliver the mixture at a rather low pressure. If platinum is present the asbestos glows for some time. When destroyed the property of glowing can be restored by heating to redness again. The test is made more intense by using warmed gas and is said to be sensitive to 0·002 mgrm of platinum, 0·005 mgrm. of iridium, 0·0009 mgrm. of rhodium, and 0·0005 mgrm. of palladium, but does not reveal the presence of osmium or ruthenium.

VARIATIONS OF THE CATALYTIC POWER IN ELECTROPLATINOSOLS.—In a previous communication, M. A. de Gregorio Rocasolano noted some observations regarding the ageing of colloids, in a study made within an interval of some days, upon the variations of their catalytic power. He continued this study, directing his work to the processes of evolution continually undergone by colloidal systems, verifying the fact in some cases that the colloids, regarded as catalysers, undergo, even in very short periods of time, intense variations in their catalytic power. In one experiment with electroplatinosols, decomposing hydrogen peroxide during 30 consecutive hours, a reaction was produced with the same electroplatinosol of 0·0016 per cent divided into two parts, one without stabilisation and the other by adding 0·3 cubic cm. of aqueous gelatin solution at the rate of 3 per cent of colloid. All the reactions studied were obtained in similar conditions. These experiments demonstrated that not only does the catalytic power of electroplatinosols vary in each case, even within very small periods of time, but that these variations are much more intense in non-stabilised colloids than in the same systems stabilised. These variations are ascribed to the incessant differences in composition (concentration in oxygen) of the dispersed particles with the conclusion that the stabiliser acts by checking the processes of constant transformation in the colloids.—*Comptes Rendus*, July 4, 1921.

ARTIFICIAL RESINS.—The various sources of artificial resins are discussed by Mr. A. Tschirch in *Seife*, Nos. 28-29, 1921. Aldehyde resins are obtained by polymerisation of acetic aldehyde under the influence of alkalies. Methylene-phenol resins, by condensation of phenols (benzophenol; cresol; naphthol) and formic aldehyde (or its derivatives trioxymethylene, paraformaldehyde, hexamethylene-tetramine) in presence of condensation agents (chiefly HCl). There are several qualities in industry, viz., a substitute for shellac which is fusible and soluble in ordinary solvents, *e.g.*, laccaine, saliretine, medolite, &c. A second variety (amber substitute) is insoluble and infusible. This resin contains more formaldehyde and often a base ($NH_3$NaOH), *e.g.*, novolac, resinite, resite, bakelite C. Various formaldehyde resins are made by condensing formaldehyde with other compounds than phenol, such as methyl diphenylamine, naphthaline, &c. Coumarone resins are the products from condensation by $SO_4H_2$ of indene and coumarone, contained in heavy benzols (boiling at 160° to 180° C.). A great number of other reactions give resinous substances, *e.g.*, the action of formic aldehyde on lactic acid from which a bone-like substance is obtained. Likewise, the lignin from sulphite liquor in cellulose manufacture gives resins for which there are already uses.—*Chimie et Industrie*, July, 1921.

## BOOKS RECEIVED.

"Bleaching." Being a *resumé* on the important researches on the industry during the years 1908-1920. By S. H. Higgins, M.Sc. Pp. viii. +137. London: Longmans Green & Co. Price 10s. 6d. net.

"An Introduction to Organic Chemistry." By D. L. L Hammick, M.A. Pp. vii.+258. London: G. Bell & Sons, Ltd. Price 6s.

"The Fixation of Atmospheric Nitrogen." By Joseph Knox, D.Sc. Second Edition. Pp. vii. +124 London: Gurney & Jackson. Price 4s net.

"Botany for Students of Medicine and Pharmacy." By F. E. Fritch, D.Sc., Ph.D., F.L S., and E. J. Sailsbury, D.Sc., F.L.S. Pp xi.+357. London: G. Bell & Sons, Ltd. Price 10s. 6d.

## New Patents.

This List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W.C.2, from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

27196—Aquazone Laboratories, Inc.—Aqueous solutions containing oxygen, and methods of producing same. October 13.
26849—Mai, A.—Process for making arsenical solutions. October 11.
27188—West, H. J.—Manufacture of hydrogen or gases rich in hydrogen. October 13.
25681—Jones, H. Sefton.—Water soluble compounds of diethyl-barbituric acid and its homologues, and manufacture of same. October 8.

*Specifications published this Week.*

146411—Wehmer, C.—Manufacture of fumaric acid.
147067—Chemische Fabrik Rhenania Akt. Ges., Stuer, B.C., and Grob, W.—Manufacture of nitrogen containing addition and condensation products from acetylene and ammonia.
147094—The te, J.—Manufacture of sulphuric acid.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

## NEW COMPANIES.

The under-mentioned particulars of New Companies recently registered are taken from the Daily Register compiled by Jordan & Sons, Limited, Company Registration Agents, Chancery Lane, W.C.2.

Booth & Openshaw (Blackburn) Limited.—(177365)—Registered October 20th, 1921. 17/19, St. Peters Street, Blackburn. To carry on the business of Chemists, Druggists, etc. Nominal Capital: £2,000 in 2,000 Shares of £1 each. Directors: W. W Openshaw, Brooklyn Road, Wilpshire, Near Blackburn; I. Turner, 30, Watling Street Road, Fulwood, Preston. Qualification of Directors: One Share. Remuneration of Directors To be voted by Company.

Chemical and Pulp Company, Limited.—(177392)—Registered October 21st, 1921. 595/596, Salisbury House, London Wall, E.C.2. To carry on the business of Dealers in Chemicals, Manures and Dyes, etc. Nominal Capital. £5,000 in 5,000 Shares of £1 each. Directors: W. S Hopkins, 63, Stratford Road, Thornton Heath, S.W., F. H. Johnson, 12, St. Wilfrid's Road, New Barnet, Herts. Qualification of Directors £100. Remuneration of Directors: To be voted by Company.

## MEETINGS FOR THE WEEK.

*Monday, November 7.*

Institution of Electrical Engineers, at 7. Discussion on "How best to speed up Electrical Progress"

*Wednesday, November 9.*

Royal Society of Arts, at 8 "The Work of the Industrial Fatigue Research Board and its Applications to Industry" by D. R. Wilson, M.A, Secretary of the Industrial Fatigue Research Board.

*Thursday, November 10.*

Optical Society, at 7.30. "The Path of Rays in Periscopes having an Inverting System comprising two Separated Lenses" by Dr. Alexander Gleichen. "The Interocular Distance" by Dr. James W. French. "Note on the Thin Astigmatic Lens" by T. Chaundy, M A.

## NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemical Apparatus, &c, for review or notice to be addressed to the Editor.

**SUBSCRIPTIONS**, £1 12s. per annum, payable in advance should be addressed to the Manager.

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## ADVERTISEMENTS.

**All communications for this Department should be addressed to—**

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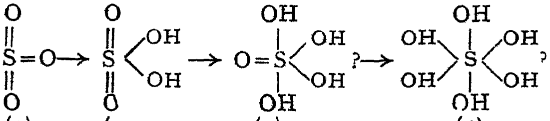
THE CHEMICAL NEWS.
VOL. CXXIII., No. 3213.

# THE HYDROXYL RING.

By H. T. F. R ,ODES.

This question has already received some attention (Rhodes, Chemical News, 19 , cx ., ), but only the general outline was considered, and it is now proposed to discuss with more detail the position of the hydroxyl ring in those salts which form hydrates, and which are wont to be described as possessing "water of crystallisation."

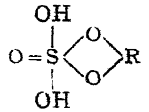
For reasons which will appear hereafter it is desirable to make allusion here to the addition products which sulphur trioxide forms with water:



(1) (2) (3) (4)

This is, of course, elementary except in the case of the last two compounds, $H_2SO_4.H_2O$ and $H_2SO_4.2H_2O$ the structures of which are doubtful, but to which allusion will again be made.

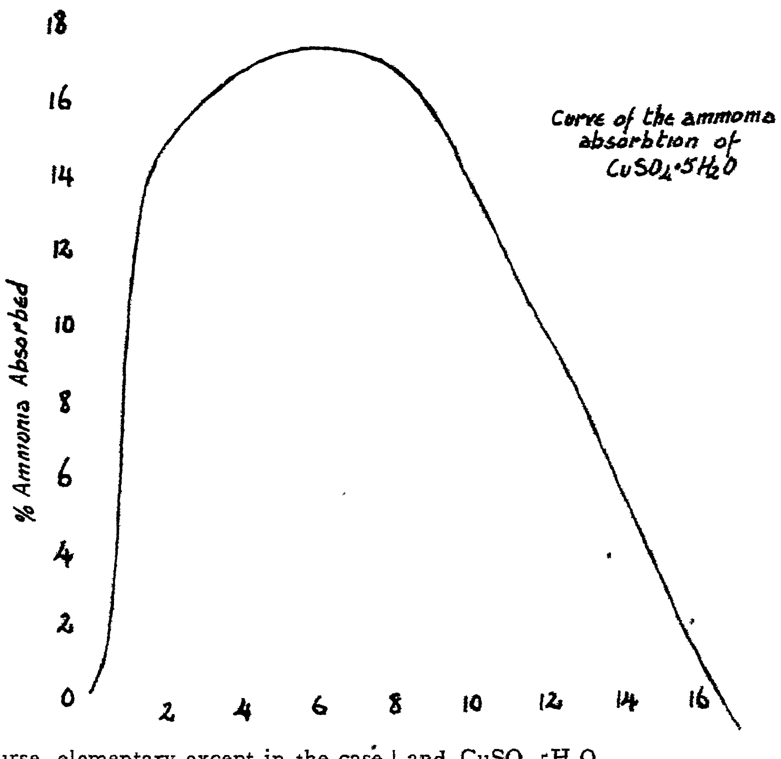
This hygroscopic quantity of sulphur trioxide will now be considered in relation to water of crystallisation. The author has already showr (Rhodes, La hygroscopisidad y el aqua de cristalisación, Universidad de Sevilla, 1920) that all salts when deprived of their water of crystallisation are hygroscopic. But it appeared probable that the mono-hydrates $XY.H_2O$ might be true hydroxyl compounds analogous to formula (3) above. This supposition—because of the higher dissociation temperature of most of the mono-hydrates—has frequently been advanced, but beyond this somewhat slender evidence, no additional facts in support of the structure



have been forthcoming.

This question was therefore made the subject of investigation (Rhodes, El Congreso de Oporto Los aminos, los hidro-aminos y los hidratos del sulfato de cobre, July, 1921).

It is, of course, a well-known fact that acqueous vapour will replace the ammonia, group for group, in the compound $CnSO_4.5NH_3$; and it was thought not improbable that the behaviour of the pentahydrate of copper sulphate in the presence of dry ammonia gas might throw some light on the relation between the compounds $CuSO_4.5NH_3$ and $CuSO_4.5H_2O$.




The action of dry ammonia gas on the penta hydrate proved to be interesting. The salt gained in weight until a compound corresponding to the formula $CuSO_4.5H_2O\ 3NH_3$ was obtained. The ammonia then began to replace the hydroxyl The final product proved to be the well-known tetrammino mono hydro cupric sulphate $CuSO_4.4NH_3.H_2O$.

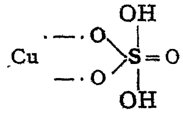
This would seem to make evident the structure of the monohydrate of copper sulphate. Water

is known to replace all the ammonia in the pentammine, but ammonia, under the same conditions can replace but four molecules of water.

It has been shown that the formula of the pentammine cupric sulphate may be represented by the structure

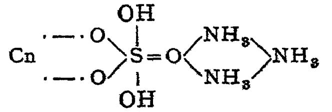
(Rhodes, El Congreso de Oporto, *loc. cit.*).

But the pentahydrate cannot be analogous to this, since only four hydroxyl groups are replacable by ammonia. The formula must therefore be represented thus:



In considering the possibilities with regard to the position of the hydroxyl ring it is necessary again to consider the compound $CuSO_4.5H_2O.3NH_3$.

This triammino pentahydro cupric sulphate would not be formed if the ammonia were associated with the hydroxyl ring, since under these circumstances direct substitution, without the formation of an intermediate, would result. The formula of this compound must therefore be



It must be admitted that this evidence in favour of the position of the hydroxyl ring is not conclusive, but it is, nevertheless, not founded upon mere hypothesis. The validity of the evidence rests upon the existence of this triammino pentahydro cupric sulphate which is an extremely unstable colloidal compound; but instability does not render unjustifiable an assumption as to its structure, and its ammonia content corresponding, as it does, to $(3NH_3)$ supports, although it does not definitely substantiate, this view. The formation of these colloidal hydroammino compounds is also an indirect but interesting confirmation of the work of Kuniloff (*Ann. Chym. Phys.*, 1906, viii., 568). Allusion has already been made to the fact that the assumption that the hydroxyl ring divides the anion and cation is in general agreement with the conclusions that Ephraim and Bolle and Ephraim and Millman (*loc. cit.*) appear to have arrived at.

But this does not dispose of a large number of other hydrates the question of whose structure has already been discussed (Rhodes, CHEMICAL NEWS, *loc. cit.*).

It has seemed desirable, in agreement with McLeod Brown (CHEMICAL NEWS, No. 2833, cix., 123) to dismiss as improbable a structure which assumes that the hydroxyl ring is attached to the oxygen atom of the anion; as well as the "gravitational" theory, which was, at best, a clumsy hypothesis.

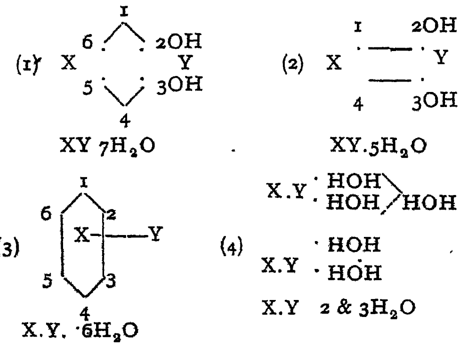
The theory of Kohlrauch (*Proc. Roy. Soc.*, 1903, lxxi., 338) concerning the mechanical retention of some metallic ions within a "shell" of water seems therefore the most satisfactory hypothesis, and its application to those hydrates containing six or twelve molecules of water seems natural and plausible.

In the present state of our knowledge, therefore, it is necessary to accept the trial hypothesis that in these cases where the hydroxyl ring does not separate anion and cation, the metallic ion is retained within a ring or shell of water.

This is an interesting view since it seems not impossible that the hydrolysis of some salts such as the chlorides of aluminium and magnesium may be effected by the presence of this hydroxyl. The abnormal behaviour of chromium and aluminium salts upon electrolysis is also possibly due to the structure of their hydrates; it is hoped that this matter will receive consideration later, but the data available at present are not sufficient to merit special notice at this time.

### *Conclusions.*

It is only necessary to add that four classes of hydrates are now recognised:



It will be found possible to classify the greater number of hydrates in this way There are, of course, exceptions, some of which have already been considered; these, however, are not numerous, and, when more data are available, they will receive special consideration.

*Note.*—The author wishes to express his thanks to Miss I. Watt, Member of the Pharmaceutical Society, and to J. H. Jackson, Esq., J.P., both of whom made it possible for him to complete his work for the Congress of Science held at Oporto in July of this year. Through circumstances over which he had no control, the writer was compelled to cut short his work at Seville University, and to complete that which remained to be done in England, under conditions of some difficulty. Both of the above most kindly lent the writer apparatus, and in general rendered him most valuable assistance.

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ROYAL INSTITUTION.—A General Monthly Meeting of the Members of the Royal Institution was held on the 7th inst.), Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Dr. W. A. Bond was elected a Member. The Special Thanks of the Members were returned to Mrs. Williams for her gift of personal notes of Davy's Lectures at the Royal Institution made by Thomas Harrison (Secretary R.I. 1818-24) and 22 books of the Works of Cicero, Horace, Hippocrates, and Waring, formerly in his possession. The Chairman reported the deaths of the Earl of Ducie, Mr. J. H. Balfour-Browne, and Professor G. Lippmann, and resolutions of condolence with the families were passed.

# THE GRAPHICAL REPRESENTATION OF CERTAIN HETEROGENEOUS EQUILIBRIA.

By A. C. D. RIVETT.

The ordinary graphical representation of solubility relations of solids (that is to say, of equilibria between solids and solutions) implies certain conclusions which cannot be justified.

In numerous text-books and treatises on the Phase Theory, as well as in original memoirs, it has become customary to represent binary systems, usually examined under an arbitrarily selected pressure sufficiently great to prevent vapour formation, by composition-temperature diagrams, of which Fig. 1 may be taken as a type

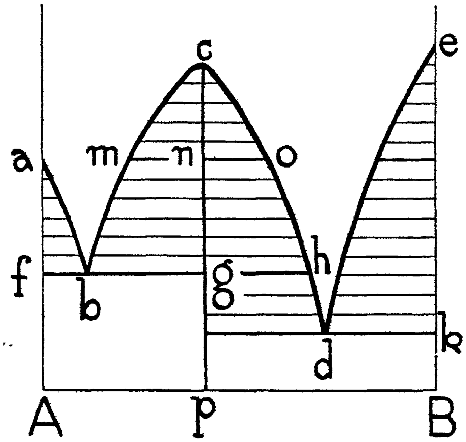



Fig. 1.

Percentage compositions (by weight, atom, or molecule, as may be preferred) are plotted along the axis of abscissæ, the respective ends of it representing pure component A or B. A point such as $p$ indicates a mixture, or may be a compound, of which $p$B per cent is component A and $p$A per cent is component B. Temperatures are plotted along the axis of ordinates.

The curve *ab* (or *ed*), termed a "solubility curve," gives solutions commonly stated to be in equilibrium with solid pure A (or B), that is, with a solid represented in composition by any point on the vertical line *af* (or *ek*). Any mixture of mean composition corresponding with a point in the area *afb* (or *edk*) will separate into pure solid A (or B) and a solution on *ab* (or *ed*).

Now in discussing the question of the immiscibility or otherwise of metals in the solid state, Alkins has pointed out (in a communication not yet published) that the Phase Rule requires variation in the solid phase in binary systems to correspond with variation in the liquid phase. The argument is that as a condensed binary system in two phases can have but one degree of freedom, therefore, with any selected solid, say pure A, there can be only one liquid in equilibrium, and that at only one particular temperature. For any other liquid the solid must have another composition, and the temperature must be different.

This conclusion is quite general. The "solubility curve of a component" is not what the description implies. The curve gives compositions of a series of solutions each in equilibrium with a separate, distinct solid. The variations in composition of the solid may be slight, but they cannot be zero. Particular cases will differ in degree only. This, which applies to the curves *ab* and *ed* of Fig. 1, applies equally to any intermediate curve such as *bcd*. *bcd* would generally be described as the curve giving all solutions which can exist in equilibrium with a definite solid compound having the composition of the turning point *c*, that is to say, with a solid represented by any point on the vertical line *cp*. If, however, it were this, it would follow that solutions *m* and *o*, for example, being each in equilibrium with the same solid (*n*), would be able to exist in equilibrium with one another. As a matter of fact, they cannot do so. In whatever proportions these liquids be brought together, a phase reaction always occurs giving a solid and more or less (in one case, none at all) of a single liquid of the same composition as one or other of them. Or again, if the interpretation quoted were correct, there would be a range of selection of temperatures at which three phases (two liquid and one solid) could co-exist. This, however, is impossible, since a three-phase condensed two-component system is invariant. Nor is it possible, as the diagram suggests, for four phases, namely, solid A (*f*), solid *p* (*g*), and the liquids *b* and *h* to be in equilibrium under an arbitrarily selected pressure.

It follows that the correct form of the general or typical diagram is of the type shown in Fig. 2.

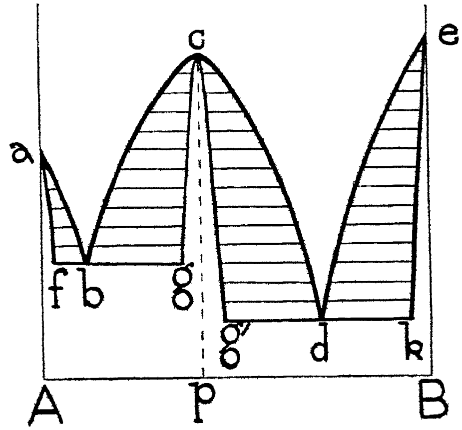



Fig. 2.

This shows that the composition of the solid phase (represented along the curves *af*, *gcg'*, or *ek*, as the case may be) varies, however little, as the composition of the liquid phase (represented along *ab*, *bcd*, or *de*, respectively) varies. Incidentally it follows that *c*, the turning-point, is only one of a series of varying solids, though one that is unique in that it has the same composition as the liquid with which it is in equilibrium, this being the necessary condition that the curve shall have a turning-point. It follows, too, that the solid which separates out during cooling of a solution saturated at an upper temperature will not be of uniform composition. The range of variation may or may not be large.

An argument quite similar in kind may be applied to ternary systems. The usual representation of a typical condensed isotherm is given in Fig. 3, where, say, A is a solvent and B and C are solid salts. B and C are assumed to form, in integral molecular proportions, a "double salt," or compound, D

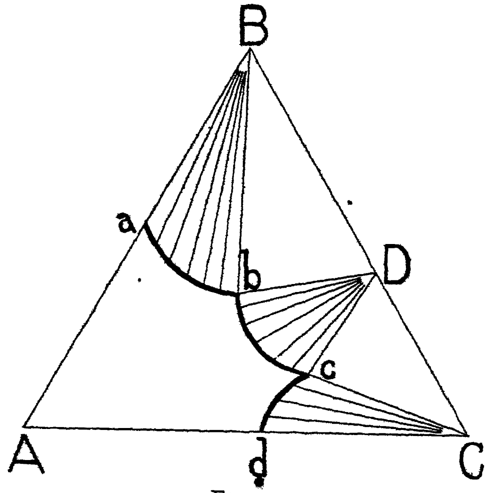



FIG. 3.

There are three curves, *ab*, *bc*, and *cd*. Now, if the system be quite rightly represented here, D, say, can be in equilibrium with a number of solutions of different compositions ranging from *b* to *c*. Therefore all such solutions must be able to exist in equilibrium with one another—an obvious absurdity. Or again, D can exist with solution *b* and solid B; also with solution *c* and solid C Hence the five phases represented, respectively, at B, D, C, *b* and *c* can exist together in a condensed system at the arbitrarily chosen temperature of the isotherm. This is in contradiction to the Phase Rule. There cannot be more

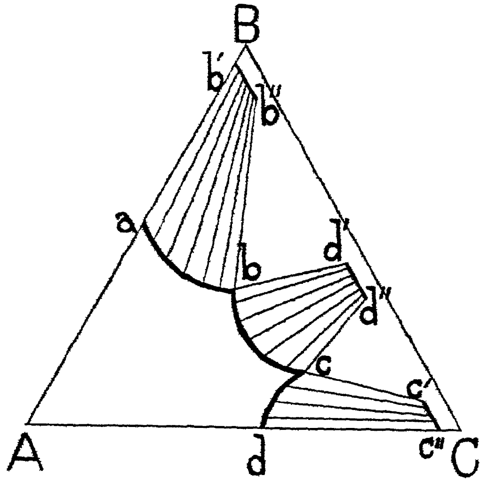



FIG. 4.

than three phases in equilibrium in a ternary system if temperature and pressure be arbitrarily fixed.

The Phase Rule, in fact, requires for this case relations such as are diagrammatically represented in Fig. 4.

Instead of the solid phases in equilibrium, respectively, with solutions along the curves *ab*, *bc*, and *cd* being represented by points B, D, and C, they must be represented by lines $b'b''$, $d'd''$, and $c'c''$, however short these lines may be; and since of course the component A also must enter into these solids, these lines will lie wholly in the ternary region except that one end of the first ($b'$) and one end of the last ($c''$) will be on the corresponding binary sides of the triangle. This then will show that there is a distinct composition of solid for every composition of liquid.

A similar argument may be applied to higher systems. Variation of solid phase with variation of liquid is the general rule, and this may be stated also in the form that mixed-crystal (or solid solution) formation is general in the solids which separate from solutions Considerations of like kind hold, of course, for phase equilibria between solids only. It is advisable not to overlook these facts in our customary diagrammatic representations of heterogeneous equilibria, since to do so implies relations which are impossible

Chemistry Department,
University of Melbourne.
September 2, 1921.

## THE CHEMIST IN THE STEEL AND IRON INDUSTRY.

### A Few Thoughts on his Experiences, Training, Status, and Influence on Manufacture.

By C H. RIDSDALE.

When you did me the honour of inviting me to give you an address, and, whilst leaving the subject open, intimated that "some reference should be made to the status of the chemist in the steel industry as it stands to-day," I felt at once that this subject itself might be worth your consideration, and that you would perhaps bear with me if, instead of giving you something technical or formal, I simply submit for your consideration a few thoughts which have been borne in on my mind from time to time in the course of my life experiences, and as to which I shall hope to learn your views in the discussion.

I suppose most of you are works' chemists—many of you in iron and steel works—and if so, you are a body of men for whom I have always had a very warm place in my heart, for although my early chemical training was in a public laboratory under Dr. Stead, and I am again back into public practice, for the intervening 37 years I was a works' chemist in the iron and steel industry, so I can claim to be one of yourselves.

In that capacity I have had the engaging and training—so far as the limited conditions of works practice permit it—of a very large number of young chemists, and have followed every detail of their progress from the boy who has just left school, onward until he has in many cases become a highly competent chemist or works' manager.

Many of you are young men setting out to

*An address given to the Glasgow Branch of the British Associat on of Chemists, October 19, 1921.

climb the ladder to fame, and I shall feel it a privilege as well as a duty if anything I can tell you will enable you to improve your position and get fuller value out of life. You can be sure I am not theorising, but giving you conclusions drawn from my own experience in a practical life, under conditions where no attempt was made "to temper the wind to the shorn lamb."

A chemist instinctively, whether conscious of it or not, analyses not only materials, but ideas and pretty well everything which comes under his observation, and, true to his instinct, whatever he finds he feels bound to report, no matter where the results lead to. This is because he who is truly a chemist at heart, and has not simply been pitchforked into it, or taken it up with the idea that it is "a nice soft job," is essentially a seeker after truth, and to a large extent, an idealist.

Mr. Pilcher, Registrar and Secretary of the Institute of Chemistry, in a book he has published, quotes Beecher's description of chemists as "a strange class of mortals, impelled by an almost insane impulse to take their pleasure among smoke and vapour, soot and flame, poison and poverty . . . . . One singular resemblance between Holy Orders and the practice of Chemistry—the practitioner is supposed to receive part payment from his temperamental delight in the subject itself."

This seems to me an apt description, and was particularly so of the chemist in the basic Bessemer shop, though in open-hearth plants, and with the present better pay, it loses some of its cogency.

Still, the chemist is often regarded by the other men in the works with a certain amount of awe, and as being associated with mystery; just as the alchemist in the old days was—like Faust, generally associated with the devil.

In my earliest steel-works experience the laboratory was known as "The Doctor's Shop," and although this designation had reference primarily to the bottles and coloured liquids, yet it soon justified the appellation, for as there was no ambulance installation, we got a collection of lint, bandages, sticking plaster, carron oil, &c., and gave first aid in cases that were not too serious, and in one year of which I kept a record, we treated 1000 cuts, burns, scalp wounds, &c. Nor was it altogether unknown for a chief chemist to keep quinine, toothache mixture, cocaine, and a few other simple medicaments for assistants having slight ailments but not wanting to leave their work.

And this reminds me that one of the most pleasing features of the chemist's profession is the wonderful variety of experiences to which it may lead. What a romance there is in the life if the proper attitude of mind is maintained! What a number of avenues open out! Why, it has never seemed to me that even a pirate's life had the glamour that a chemist's offers. And surely horse-racing cannot offer more thrills than the intensely eager interest with which one awaits the result of the referee chemist's finding in an important dispute case.

I dare not commence to give you any of my own reminiscences, or I should go on too long and weary you. But to get this feeling of romance, one must take the right interest in one's work. The man who takes a keen interest in, or is enthusiastic about his work, not only turns it into a sport, but materially adds to his own worth.

Every employer values one who does so much more highly, and will, when it comes to a test, give better pay or privilege to retain him.

There is, of course, some monotony and drudgery. All work has it. In fact, nothing really great is achieved without it. Remember, "*Per Ardua ad Astra.*" Works' chemists have great responsibility; for instance, even junior assistants are held responsible for the passing on their analyses of large casts of steel, a single one of which during the war might be worth £1,000.

The work of the chief chemist may cover an enormous range which I cannot attempt to enumerate, but they have to deal with the acceptance of raw materials and the passing for despatch of manufactured materials which in one year may be worth millions of pounds, and have also the technical control throughout manufacture It has seemed to me that on the Continent their importance is generally more fully recognised than here, and their position ranks higher. I doubt if anyone gets a more thorough knowledge of what is going on throughout a works than the chief chemist.

Chemists have to deal with materials and forces—and use them as tools or weapons—which may be very dangerous if handled carelessly, though they are not dangerous if handled with proper knowledge and judgment. It is the *balance* and correct sense of proportion acquired by the nature of their training which should render their influence so valuable as they mix in the world, and which should automatically become disseminated amongst those around them.

Meanwhile, I think you will all agree that chemists not only are of great use in the world, but could be of still more use if it would learn how to avail itself more fully of their services, and they must try to show it how to do this.

You will, I feel sure, agree too, that the status ought to be improved. Let us see exactly what status means.

My dictionary—and therefore, of course, the best—defines it as "condition, social standing or place, rank." You will note it is not primarily a question of money—and I think for our purpose it might be expressed as the good opinion or *value which others spontaneously accord*—for you cannot force spontaneous good opinion.

Now the chemist's value is not simply measured according to his *technical* ability. One great value, inculcated both by the essential nature of his training and occupation, is the *attitude of mind* which these, perhaps more than in any other profession, tend to induce and develop—precision, accuracy, reliability, truth, and resourcefulness. In short, his mental attitude may be one of the main factors in the improvement of the status of the chemist.

The power and value of a right mental outlook and of other things which may seem irrelevant have been realised more and more of late by hard-headed practical men, hence we now have all sorts of psychological questions which a few years ago were rarely mentioned or thought of as connected with business, seriously studied and set forth—for example, questions of fatigue, and welfare work generally.

As this address has for its primary object the

welfare of the iron and steel works' chemist, I ask you to bear with me in my mention of some of such questions.

I suppose, looked at broadly, each of the chemical societies aims at doing a sort of welfare work for the particular section it represents. I only give a brief impression of the outstanding features which differentiate them.

*The Chemical Society,* by eliciting, collecting, and publishing for the use of its members, papers, new facts, and researches, covers practically the whole range of pure chemistry.

*The Society of Chemical Industry* by doing the same, chiefly with regard to the *industrial* application of chemistry.

*The Society of Public Analysts* devotes itself mainly to the progress of *analytical* chemistry.

*The Institute of Chemistry,* being "primarily a certifying body (*Proceedings,* Part II., April, 1918, p. 39), as such seeks to elevate the profession; *first,* by setting up a particular standard for admission, which it expects will obtain from the public, recognition that its members are of a somewhat higher status than those who are not members, and, as a gauge for which, it holds examinations; *secondly,* by indicating a precise course of training which prospective candidates should undergo to fit them to meet that standard; and *thirdly,* by suggesting minimum rates of payment for certain positions, keeping an appointments' register, and in similar ways endeavouring to benefit members financially. Those who wish to be regarded by the Institute as reaching its standards are required to present themselves for examination, or to satisfy it in some other specified way.

As regards these methods, the *first* especially, seems to me to entail a difficulty which might be compared to that met with when using a square-meshed sieve to separate small material from larger; a great deal of small is removed, but also it often happens that an appreciable proportion of pieces which have quite as much volume and weight as the average piece left on—and sometimes more— are not retained, but rejected with the small, just because they are of a less usual shape than the average lumps.

They may even be pieces two or three times as long, and heavier than more cube-shaped pieces retained, but they are lost just because they were undersized in one particular dimension, and would perhaps just go through corner-wise. So too, on the other hand, in spite of careful sieving, a certain number of pieces *smaller* than are wanted are inevitably retained.

It would seem quite reasonable from its own stand-point that any society should make its own rules for admission to it, and for gauging the qualifications of prospective members, but when it seeks, or tends to become, a measure of qualifications generally in that particular line, then those who believe themselves to be equally qualified, but for reasons which they consider adequate, do not or cannot comply with the prescribed conditions, perhaps not unnaturally feel aggrieved, as they are subjected automatically to an implication of lower status. I know this is the view of some industrial chemists holding important positions. Thus, in the Institute's case, having a Charter, and its dictum carrying a certain weight, it naturally draws criticism not directed to societies the procedure of which does not bring about similar differentiation. This is the more so because there are some members who would go even further, and strongly advocate making analytical chemistry a close profession.

(To be continued

## TRAINING FOR FOREIGN EXPLORATION.*

By H. FOSTER BAIN,

Director United States Bureau of Mines.

(Concluded from p. 245)

MINERALS are the raw materials on which are based numerous industries and the conditions which limit their use are the same in many particulars as are those which unduly aid industry in a given region. Security of title, stability of government, availability of labour, adequacy of financial support, these are all matters to be considered by economists. Here again the exploring engineer may to his own advantage draw on a fellow professional for methods and data. His own training prepares him to judge as to the material. Matters concerning men and money are, however, equally important, since the test of his results is whether he has found something which may be produced with reasonable expectation of profit. The subject is too large for discussion here. I may merely mention a few items by way of illustration.

One of the assumptions too commonly made is that low wages necessarily means cheap production. This may or may not be true. It is largely a matter of efficiency. It it requires, as it sometimes does, six miners of one race to do the work of one of another, it must be clear that paying wages in the ratio of one to six does not lower costs. Not only that, but the final cost of production with such "cheap" labour will be higher because of the larger number of working faces necessary in the mine, greater amount of equipment, the extra supervision and housing, the higher accident ratio and other matters, all of which enter into the final cost. On the contrary, one must not conclude that raising wages cheapens production. It only does so when increased efficiency results from the added desire on the part of the men to hold their jobs, or when it enables a particular employer to attract the better men from others. Generally, added efficiency in labour is purchased at an increased cost per unit, just as the added speed of a fast steamer calls for more coal per mile than when driving at a slower rate. It is also to be remembered that there are natural inequalities in efficiency and in the economical rate of speed of work as between men. These can only be changed slowly. Another factor to be constantly kept in mind by the engineer is that one of the costs of a new enterprise is that of attracting labour to it from existing industries. It may usually be safely assumed that the people of any district are already employed. If they do not work they generally starve. What they are doing may seem relatively unimportant to the visitor, but it assumes another

* Forty-eighth Annual Commencement Address, delivered on April 29, 1921, and reprinted from the *Bulletin* of the School of Mines and Metallurgy, University of Missouri, June, 1921, No. 3, vol. xiii.

aspect to them. It is necessary either to import men already accustomed to the industry, usually at material expense, or to tempt workers out of some other line into the new one, and then to train them to it. This requires both time and money. The importance of the time factor arises from its effect on the present value of proposed investment. To illustrate: deferring the initial returns for two years decreases by 14 per cent the present value of a series of dividends running through 20 years at 8 per cent, assuming accumulations at 3 per cent. The actual result varies with the assumption of time and rate, but the essential fact is that mere delay is expensive. When this delay is coupled with upkeep charges it is even more serious. This whole matter of the possible and probable rate of continuity of production is one of first importance in determining the availability or value of any mine or prospect. Into it enters also the various questions of market. I have already indicated my reasons for believing that, whatever may be the depressing facts of the immediate present, we may safely assume a continued demand for metals. This demand will, however, vary from time to time both for the group as a whole, such variations being due to general causes outside the industry itself, and also as relates to each metal It is necessary to study problems such as expansion of use, substitution, periodic demand, and similar matters far aside from ordinary class-room instruction. As regards a particular enterprise, it is necessary in fixing capitalisation to make assumptions not only as to the probable average price of output during the life-time of the investment but also the maximum and minimum to be assumed, the probable period of duration of each, and if, as is occasionally true, some guess can be made as to the impending swing of the pendulum, it will be of great assistance. A property is financed on the basis of average returns through an expected life determined by consideration of numerous factors. A company in which capital is so adjusted to income may nevertheless fail if not prepared to withstand a temporary period of low prices, while if high prices may be safely assumed in the near future it is possible to finance the enterprise from earnings to a considerable extent. There is one general rule—the old one, that a "bird in hand is worth two in bush." This is sound, not only because of the risk attached to the question of acquiring the two theoretically in the bush, but because the one in hand, if a good hen, may lay eggs through the waiting period. The dollar of to-day is worth more, normally, than the dollar which is to be paid some years later because it may earn for you interest meanwhile. This principle of the greater value of quick returns when astutely used is a great help in bargaining.

It happens that there are many minerals that are only of important value when properly related to others. Iron ore, coking coal, and limestone form a trinity. Nothing is of less value than a large deposit of pure iron where it cannot be used. The value of iron ore is less a matter of the extent and composition of the deposit than the assembly cost of raw materials at a suitable point for making pig iron and steel. Such matters seem, possibly, far from the province of the exploring engineer, but all around the world are wrecks of business enterprises where money was spent to find and develop raw materials without adequate study of competition and market conditions. The exploring engineer who disregards such problems limits his usefulness and the rewards that he may expect

Just as any engineer starting for a far country carries in addition to instruments, food, and engineering supplies, a personal kit, so there are accomplishments that are as desirable if not necessary to the exploring engineer as his knowledge of mathematics and geology. He must know how to keep himself and his men in good health or his expedition will fail. He is the scout of industry and often the pioneer of civilisation. When he goes into the wilds the health risk is often the greatest personal danger faced. Even when he goes to older settled countries the conditions of life differ from those in his own home, and care is necessary. With care it is possible to live and work in almost any country. It is now known that where it is worth while to do so, even tropical jungle lands may be made safe and sanitary. To do this involves heavy expenditure not warranted in exploration, so that the pioneers assume risks not necessarily met by the operating forces that come later. The exploring engineer would do well to look carefully to his own physical condition, and watch closely the food, drink, and habits of his party. Learn and enforce proper rules as to camp sanitation. One careless man may wreck an expedition or cause long and expensive delays. It is generally true that the most suitable food is the food of the country, but the exceptions are numerous and the cost of a mistake serious. Until the facts in each instance are established, it is a justifiable expense to use imported foods. Proper cooking will render foods otherwise dangerous safe, and moderation in eating strange dishes is a wise precaution. The American habit of drinking raw water is one to be indulged with discretion in regions of older civilisations, but safe water is easily obtained by boiling. It is worth while to pay attention to details such as these which seem small to those accustomed to our own ways of living. A knowledge of the methods of first aid and a few medicines is of great value. It is not necessary to go as far as Doc Milliken who, as you may remember, would "take that bracket saw and the mild chloride and his hypodermic, and treat anything from yellow fever to a personal friend," but a little knowledge of simple medicines will ease your way greatly in strange countries. Learn to ride, to shoot, to swim, and to handle a small boat. I need hardly admonish a young American these days to learn to run a motor-car, but the accomplishments common in the older days of country and village life are becoming rare. It is not always possible to ride up to a prospect in a Pullman or even in a Ford. In the nature of things, the finding of new mines will take one into countries where only other than mining industries have been developed, and in practice that means going into regions of country and village life. At times it means rolling back the centuries and living for awhile in the mediæval ages. In such places one must know about horses and mules—their habits, preferences, food, simple ailments, and capacities for work. One may, too, be called upon to use a gun, though far more probably to afford the party fresh meat

than as a means of protection. To handle a boat or to swim may be a necessity at any time, though it must be admitted that in any country where small boats are used native boatmen are likely to be numerous and skilful. Skill in any of the forms of what we now call sport may well prove of first importance in an emergency and will always prove at once a means of relaxation and of establishing relations with strangers, regardless of race and language. The latter is a matter of no small importance in work when the goodwill of the whole party and of the people of the country traversed is so important.

Lastly, I would urge that to be successful one should have something of the spirit of adventure Unless new scenes and new faces appeal to you, unless you find joy in the long days in the saddle or afoot, unless the cheer of the camp fire means more to you than the clank of the steam radiator, unless to you coffee does not lose its fine flavour when served in a tin cup, unless you can sleep between blankets and not think of their scratching, do not undertake exploration. If you must have a napkin and morning paper at breakfast, if you cannot write save at a well-equipped desk, if you are not happy except with your family and intimate friends, if you must needs see the movies before you can go to bed at night, you will be wise to find a routine job at home. But to those who have a venturing nature adventures come, and if you are one of the elect who feel the spell of the Yukon, or the lure of the little voices, then go

"Adventuring! Adventuring! And oh, the sights to see
And little fires along the trail that wink at you and me,
Till the last adventure calls from the old, the vain desires,
To a way that's still untrodden, though aglow with little fires,
Where no wanderer grows weary and a man is free to roam,
Or hang his hat upon a star and call the planet home."

## NITROGENOUS MANURES.

### *The Action of the Manures.*

Nitrogenous manures have more striking effects than any others in increasing the growth of farm crops. Under normal circumstances a dressing applied at the proper time produces visible results almost in a few days: the plant becomes greener, stands up well, and starts into growth, while the untreated portions of the same crop are unchanged. It has often happened that a dressing of 1cwt. per acre of nitrate of soda or sulphate of ammonia has given an additional 4 bushels of wheat or 6 bushels of oats.

Experience has shown that nitrogenous manures are effective in several directions.

1. *On Winter Corn after a Wet Winter.*—In this case a top-dressing of 1 to 1½cwt. per acre of nitrate of soda or sulphate of ammonia should be given in spring as early as convenient. One must not, of course, go on to the land until it is sufficiently dry to bear the distributor without injury, nor should the manure be applied to winter corn in frosty weather; an opportunity should be found, however, at the end of February or early in March. If the land is sticky, 1cwt. of superphosphate per acre should be applied in addition.

There has been considerable discussion as to the most suitable quantity of nitrogenous manure to use for spring dressings for winter crops. It was formerly supposed that the most profitable returns were obtained from small dressings: more recently, however, it has been shown that moderately large dressings are more profitable—1½cwt. of nitrate of soda or sulphate of ammonia giving not only a larger, but a more profitablle crop than ¾cwt. per acre.

2. *On Spring Oats, especially in Wet Weather, or in Cold or Backward Districts.*—In this case it is necessary to add superphosphate as well: the dressing would be 1cwt. nitrate of soda or sulphate of ammonia, and 2½cwt. superphosphate per acre; or if the conditions allow of heavy crops, 1½cwt. of nitrate of soda or sulphate of ammonia, and 3cwt. superphosphate per acre

3. *On a Second Corn Crop.*—Farmers are often so anxious to avoid overmanuring their barley that they grow it as a second corn crop after wheat or oats. It frequently happens, however, that an additional yield can be obtained without sacrifice of quality by means of a moderate dressing (¾ to 1cwt.) of sulphate of ammonia, combined if need be with 2cwt. superphosphate per acre.

4. *For Potatoes and Mangolds.*—These crops practically always benefit by the use of nitrogenous manures, even when dung has been applied on a fairly liberal scale: potatoes commonly respond to 1 to 2cwt. sulphate of ammonia applied at the time of planting, while mangolds can do with the same amount of nitrate of soda, half being given when the plants are up, and half at the time of singling. Swedes and turnips, however, are less certain in their response, and frequently farmyard manure alone proves as effective as anything.

5. *Hay* practically always responds to nitrogenous manures (1½cwt. per acre), though the quality suffers unless potash and phosphates are also added.

### *What the Manures are.*

*Nitrate of Soda.*—This is the most rapid in action of the nitrogenous manures in common use, and it has repeatedly proved effective in encouraging growth in a cold spring when the young crop is beginning to turn yellow.

The speedy action is of great advantage in helping a crop over an attack by insects or wireworms; the additional nitrogen enables the plant to keep growing and thus to replace the tissue destroyed by the insects. But while nitrogenous manure is of value against insect pests it does not help against fungi; a soft sappy growth tends to develop which readily succumbs to fungus attacks.

Besides being the most rapid in action, nitrate of soda is in general the most effective, except for potatoes, for which sulphate of ammonia is better. For winter corn and for hay, nitrate of soda is about 5 per cent more effective than sulphate of ammonia; for mangolds the difference is even greater as the soda is distinctly helpful to the crop. It has the drawback that it cannot easily be used on heavy soils as it tends to make them sticky, thereby increasing the difficulty of working; further, it is not required on fen soils. Otherwise it can be used on all classes of soils, even those which are deficient in lime.

*Nitrate of Lime* is as quick in action and as effective as nitrate of soda, but it is somewhat less convenient in use owing to its tendency to take up moisture which necessitates transportation in casks. It has the advantage, however, that it can quite well be used on heavy land without pro-

ducing the stickiness caused by nitrate of soda.

*Nitrate of Ammonia* is not generally obtainable at present, though it is understood that its manufacture is being undertaken by an important industrial organisation. It is more rapid in action and more concentrated than either of the preceding fertilisers, but it is also less convenient, tending to cake rather badly, and requiring to be stored always in casks.

*Sulphate of Ammonia* became very well known to farmers during the war from the circumstance that it is a home-made product, and was therefore obtainable long after the imported nitrates were out of the farmers' reach. Taking a general average of soils and of crops it is about 5 per cent less effective than nitrate of soda when applied on an equal nitrogen basis It is, however, more concentrated than nitrate of soda, and this more than balances its reduced efficiency, so that for equal weights it is often superior. Thus, if a farmer can buy sulphate of ammonia at the same price per ton as nitrate of soda he will in many cases save money by doing so; but if the prices are not the same, he must work out the unit price from the data given below. These statements as to averages require considerable modification when one deals with particular soils. On chalky land, sulphate of ammonia is practically equal to nitrate of soda in effectiveness; on clay soils it is preferable as it does not cause stickiness. But in peat soils and on sandy soils deficient in lime (as many of them are) it is unsafe until sufficient lime has been added: there have been cases, notably at Woburn, where sulphate of ammonia has done actual harm to the crop through its property of inducing acidity in the soil (The remarks as to acidity apply to the use of ordinary sulphate of ammonia, which is slightly acid. A "neutral" brand of less than 0·025 per cent acidity is now obtainable in certain districts, which possesses the further advantage of being drier and in better condition for distribution). The trouble can be entirely remedied by a dressing of lime, which in any case is desirable on light soils. Potatoes and oats are less affected by this acidity than other crops, indeed potatoes gain rather than lose since the scab is thereby kept in check. Any scheme for adding lime to counteract the acidity should be brought into operation just after potatoes have been removed and just before clover is to be sown.

*Muriate of Ammonia.*—It is probable that this substance will be produced on a large scale in England at an early date, and careful experiments have been undertaken to ascertain its precise fertiliser value.

*Nitrolim.*—This substance was carefully tested as a fertiliser before the war, and found to be somewhat inferior to sulphate of ammonia, besides being slower in action; further, it is not suited for top-dressings. Experiment has shown that it is not immediately available for plants, but has to undergo decomposition in the soil. It seems probable that the decomposition could usefully be brought about in the factory, thus giving a product that would be more rapid and effective in action and suitable for top-dressings.

*Storage of Nitrogenous Manures.*

The keeping qualities of nitrate of lime and nitrate of ammonia have been referred to above. Both should be kept in a dry place in the original casks. After the packages are opened, these manures cannot well be stored. Nitrate of soda may be kept for a considerable time under dry conditions in a well-built shed. It may become lumpy owing to the action of moisture and must then be crushed. Sulphate of ammonia is best stored in bags placed on planks or on a layer of peat rather than on the bare earth or a brick floor. The building in which it is stored should be dry and free from damp. The well-made "neutral" sulphate is less affected by moisture than the ordinary quality. If sulphate of ammonia should cake, it should be broken up with a wooden crusher.

*Table showing Percentage of Nitrogen in the Ordinary Nitrogenous Manures.*

| Substance | Per cent nitrogen usually present. |
|---|---|
| Nitrate of soda | $15\frac{1}{2}$ |
| Nitrate of lime | 13 |
| Nitrate of ammonia | $34\frac{1}{2}$-$35\frac{1}{2}$ |
| Sulphate of ammonia | $20\frac{1}{2}$ |
| Muriate of ammonia | 25 |
| Nitrolim | $14\frac{1}{2}$-$15\frac{1}{2}$ |

Under the Fertilisers and Feeding Stuffs Act, the percentage of nitrogen in a fertiliser must always be stated in the invoice: percentages of ammonia, sulphate of ammonia, &c., should be disregarded.

It is imperative that nitrogenous manures should be in fine condition before being applied to the land: any lumps should be sifted out and broken with a wooden rammer. Modern sulphate of ammonia of the "neutral" brand is often in better condition than the older material.

Of the manures described above, sulphate of ammonia and muriate of ammonia are the only ones which can readily be mixed with superphosphate. Where necessary nitrate of soda and superphosphate can be mixed provided both materials are dry and the mixture is used at once.

—Ministry of Agriculture, Leaflet No. 370.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

*Ordinary Meeting, November 3, 1921.*

PROF. C. S. SHERRINGTON, President, in the Chair.

THE following papers were read :—

*"Spectra of Lead Isotopes."* By T. R. MERTON, F.R.S

A comparison has been made of the wave-lengths of five lines in the spectra of ordinary lead and lead from Australian carnotite. The differences in wave-length which have been observed are not constant, but vary for the different lines. In the case of the principal line, $\lambda = 4058$ A, the difference in wave-length observed is about two hundred times as great as would be expected on theoretical grounds.

*"Experiments with Rotating Fluids."* By G. I TAYLOR, F.R.S.

Experiments in which spheres, cylinders, and vortex rings move through rotating fluids have previously been described by the author. Methods

are now described by means of which the experiments can be projected in a lantern. Instantaneous photographs taken while the experiments were in progress are shown.

Further experiments are described in which predictions from hydrodynamical theory are verified. It is shown that if any small motion be given to a rotating fluid, the resulting flow will be of such a nature that concentrated masses of coloured liquid should be drawn out into thin films, which should remain always parallel to the axis of rotation. Photographs taken by a camera placed vertically above a rotating basin of water show that a liquid does actually move in the way predicted, the films of colouring matter appearing as thin lines to an eye situated on the axis of rotation. These sheets of colouring matter may become so thin that it is only possible to see that the colour is not uniformly diffused through the liquid by placing one's eye on the axis of rotation.

*"The Two-dimensional Slow Motion of Viscous Fluids."* By L. Bairstow, F.R.S., Miss B. M. Cave, and Miss E. D. Lang.

The paper is part of a general investigation of the solution of the equations of motion of a viscous fluid. In its restricted form the equation to be solved is $\nabla^4\psi=0$, where $\psi$ is Stokes' stream function. The boundary conditions are those which give no relative motion between a solid and fluid in contact with it. If the molecular rotation in the fluid be defined by $\xi\equiv\nabla^2\psi$ it will be seen that the equation of motion may be expressed alternatively as $\nabla^2\xi=0$. An earlier paper by one of us shows how, for certain boundary conditions, an equation of the type $\nabla^2\xi=0$ may be solved in terms of simple sources distributed round the boundaries. An extension is easily made to cover the representation in terms of doublets, the finding of the strength of which has been the object of the present analysis.

The equation $\nabla^4\psi=0$ is transformed by means of Green's theorem to a form in which the only unknown is the distribution of the $\xi$ doublets on the boundaries. The strengths of the doublets is found by solving the resulting integral equation.

An example shows the motion of fluid past a circular cylinder in an infinite parallel-walled channel. Stream lines and lines of constant molecular rotation have been drawn. If $d$ be the diameter of the cylinder, $\rho$ the density of the fluid, $\nu$ the kinematic coefficient of viscosity, and U the velocity of the fluid in the centre of the channel at infinity, then, when the width of the channel is $5d$, the resistance per unit length of cylinder is $R=7{\cdot}10\ \rho\nu d U$. The value of $Ud/\nu$ to which this formula applies is not to exceed 0·2.

*"Production of Single Crystals of Aluminium and their Tensile Properties."* By H. C. H. Carpenter, F.R.S., and Constance Elam.

An account is given of methods whereby small allotriomorphic crystals in aluminium sheets and bars have been converted into a single crystal. The parallel portion of the test pieces of the sheet was 4in.×1in.×0·125in. The conversion of this area into a single crystal involved three processes: (1) heat treatment for six hours at 550° C.; (2) application of tensile stress of 2·4 tons per square inch, producing an average elongation of 1·6 per cent on 3in.; and (3) a final heat treatment beginning at 450° and extending up to 600° C. The number of crystals present originally in the volume mentioned was about 1,687,000. Under above conditions, on an average one test piece in four produces a single crystal over its parallel portion, which frequently grows up into the shoulders of the test piece. This occupied a volume of about 0·5 cubic inch.

The tensile properties of the single crystals were determined. Considerable variations in the method of extension and fracture and the numerical values of the results were found. The tenacity of single crystals varied from 2·8 to 4·08 tons per square inch, while the extension on 3in. varied from 34 to 86 per cent. according to the orientation of crystal relative to stress. Differences in above properties have enabled specimens to be classified under five types The results of the stress tests of test pieces consisting of two crystals and also of three crystals are given. These show the strengthening influence of one crystal upon another.

Later experiments conducted on round bars resulted in the production of single crystals in the parallel portion of bars 0·564 and 0·798in. in diameter. In the former case the total volume occupied by the crystal was rather more than 1 cubic inch, while in the latter it exceeded 2 cubic inches. The tensile properties of these crystals were also determined, and it was found that in every case a wedge-shaped fracture was produced, the bar diminishing principally in one dimension only. Remarkable twinning effects were observed in certain cases.

*"Transmission Colours of Sulphur Suspensions."* By C. V. Raman and B. Ray.

When a few drops of sulphuric acid are added to a dilute solution of sodium thiosulphate and a precipitate of sulphur gradually forms in the liquid, the light transmitted through the turbid medium undergoes remarkable changes in colour and intensity. The suspension becomes practically opaque to the shorter wave-lengths first and the longer wave-lengths later, and subsequently regains its transparency partially, the shorter wave-lengths re-appearing first and later the longer wave-lengths. In the present paper, the work of Keen and Porter and of Lord Rayleigh on the subject is discussed, and it is shown how the foregoing facts may be explained on a theoretical basis.

*"Law of Distribution of Particles in Colloidal Solution."* By E. F. Burton and Miss E. Bishop.

## SOCIETY OF PUBLIC ANALYSTS.

*Ordinary Meeting, November 2, 1921.*

Held at the Chemical Society's Rooms, Burlington House.

Mr. Alfred Smetham, President in the Chair.

Certificates were read for the first time in favour of Messrs. Jack Cecil Drummond, D.Sc. (Lond.), F.I.C., Alfred William Long, John Charles Mellersh, Charles Harold Wright, M.A. (Cantab.), F.I.C.

The following were elected Members of the Society: Messrs. James Frederick Fothergill Rowlanad, B.A. (Cantab), A.I.C., William Norman Stokoe, B.Sc. (Lond.), A.I.C.

The following papers were read:—

*"The Testing of Foodstuffs for Vitamins."* By J. C. DRUMMOND, D.Sc., F.I.C., and A. F. WATSON, B.Sc., A.I.C.

The authors suggested that sooner or later analysts must seriously consider the standardisation of methods for ascertaining the value of foodstuffs as sources of those unidentified dietary units—vitamins. They stated that there is already a big demand for information on the testing of food products, but unfortunately as yet the chemical nature of the vitamins is not sufficiently understood to enable chemical or physical methods of estimation to be employed, and for the present the biological method is necessarily utilised. The many sources of error in such a method were pointed out, particularly those caused by the variability of response in individual animals, and the influence of external factors; although the authors noted that these have been considerably reduced by recent improvements in technique.

Good equipment and organisation of the feeding laboratory and scrupulous care in preparing the "pure" foods for the basal diet were shown to be essential, and the practice in the authors' laboratory was described in detail, illustrated by lantern slides.

The authors then dealt with the testing of foodstuffs for the three recognised substances of the vitamin "class," and demonstrated the type of result obtained. In conclusion, they showed the value of the method in studying the seasonal variation in the food value of butters and milk, and discussed the significance of these new discoveries from the analyst's point of view.

*"An Improved Specific Gravity Apparatus."* By C. BUTLER SAVORY, M.D., M.Ch.

The author demonstrated a new and efficient instrument for the determination of the specific gravities, which has a range from 0·2 to 1·9, and obtains direct results without calculation, to four decimal points.

## CORRESPONDENCE.

### ROYAL SOCIETY.

*To the Editor of the Chemical News.*

SIR,—You probably know that the Society possesses a collection of engravings and photographs of Fellows of considerable interest. The President and Council wish to continue the collection on the lines which have been adopted by the Trustees of the National Portrait Gallery, namely, by photographs uniform in size and character, which will be stored and catalogued; and arrangements have been made with Messrs. Russell & Sons, 73, Baker Street, W.1, by which they will take a photograph (by appointment) of any Fellow, free of charge, and deposit a copy with the Society.

The President and Council hope that those Fellows, who have not within the last two or three years given a sitting to Messrs. Russell, will assist in making the collection complete by arranging for a sitting as soon as possible.—We are, &c.,

W. B. HARDY,
J. H. JEANS,
*Secretaries, R.S.*

## New Patents.

THIS List is specially compiled for the *Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, W.C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Specifications published this Week.*

170022—Seldon, J. M. and Seldon & Co.—Catalytic oxidation processes.

149319—Linienfeld, L.—Process for the manufacture of compositions of matter and technical products containing ethers of carbohydrates having the empirical formula $n\ (C_6H_{10}O_5)$ their conversion products, and derivatives.

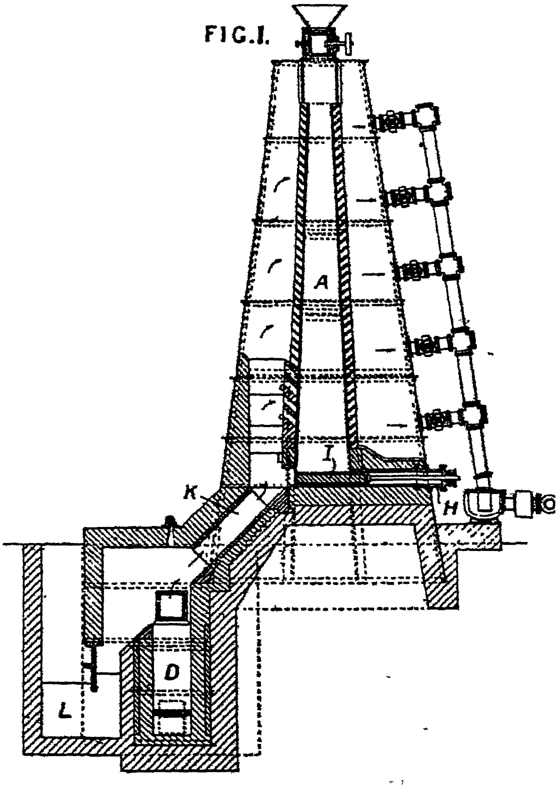
170056—British Dye-stuffs Corporation, Ltd., Green, A. G. and Herbert, A. E.—Manufacture of chlorinated derivatives of toluene.

170155—Carpmael, W.—Manufacture of new soluble chromium lakes of azodyes.

*Abstract Published this Week.*

*Gas Manufacture.*—Patent No. 167822.—Some improvements in Gas manufacturing plants have been Patented by Mr. W. P. Perry, of 19, Lytton Road, Leytonstone, London, which are illustrated in the accompanying diagram. The carbonaceous material distilled in a chamber A by the pass age there-through of hot gases from a producer D is discharged down a sloping conduit K into the producer, any surplus fuel passing over the top of the fuel in the producer and into the chamber L from which it may be lifted by an endless screw. Two plungers I working alternately from a casing H may be used, the plungers filling the casing so that no fuel can enter the casing and interfere with their action.

FIG. I.



Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

## MEETINGS FOR THE WEEK.

*Wednesday, November 16.*

Royal Society of Arts, 4.30. "Modern Buildings in Cambridge and their Architecture," by T. H. Lyon.

Society of Glass Technology, 2.30 (at Leeds). "Gas Reversing Valve for Regenerative Furnaces," by F. W. Knowles Discussion on "The Melting of Glass."

Institution of Electrical Engineers, 6. "Telephone Line Work in the United States," by E. S. Byng.

*Thursday, November 17.*

Royal Society, 4.30. "The Design of Repeating Patterns" by Major P. A. MacMahon and W. P D. MacMahon. "A Problem in the Theory of Heat Conduction" by Prof. J. W. Nicholson. "The Thermal Stresses in spherical Shells concentrically heated" by Prof. C. H. Lees. "Mathematical Foundations of Theoretical Statistics" by R. A. Fisher. "The Diffraction of Plane Electromagnetic Waves by a perfectly reflecting Sphere" by F. P. White. "On the Whispering Gallery Phenomenon" by C. V. Raman and G. A. Sutherland.

Chemical Society, 8. "The influence of nitro-groups on the reactivity of substituents in the benzene nucleus. Part V. Heteronucleal dinitro-derivatives" by H. Burton and J Kenner. "Organo-derivatives of bismuth. Part V. The stability of halogen, cyano- and thiocyano-derivatives of tertiary aromatic bismuthines" by F. Challenger and J F Wilkinson. "Organo-derivatives of bismuth. Part VI. The preparation and properties of tertiary aromatic bismuthines and their interaction with organic and inorganic halogen compounds" by F. Challenger and L. R. Ridgway.

## NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemical Apparatus, &c., for review or notice to be addressed to the Editor.

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THE CHEMICAL NEWS.
VOL. CXXIII., No. 3214.

## THE CHEMIST IN THE STEEL AND IRON INDUSTRY.

### A Few Thoughts on his Experiences, Training, Status, and Influence on Manufacture.

By C H. RIDSDALE.

(Concluded from p. 254)

THE *second* method—namely, of indicating the training—would appear good for the purpose in view, and no objection could be taken to it if every would-be candidate had an equal opportunity to undergo such training, but many, otherwise fitted, are so circumstanced through no fault of their own, that this is impossible. It seems hard on a youth earning his own living if he is ruled out, for instance, from a merely geographical reason, namely, that he lives too far from the nearest training centre.

I am not criticising the Institute's arrangements but merely looking at them from the candidate's point of view, and must admit that it is not much comfort to be told that:—

"The Council, having made provision for the admission of *all* suitable candidates to the membership, are *unable to concern themselves* with those who neglect the *many* opportunities afforded them for obtaining adequate training."—Editorial, *Proceedings*, Part V., October, 1920, p. 278.

The difficulties of special cases are no doubt recognised by many of the Fellows of the Institute, and endeavours are being made to extend facilities to meet them, and in the address of the retiring President, Sir James J. Dobbie (*Proceedings*, Part II., April, 1918, p. 40), with reference to some who decline to take the Institute's examination, and of whom, members who have passed it say: "Why should we trouble about those who decline? If they will not come in on the usual terms let them stay away. So much the worse for them." He says: "Unfortunately that is what *has* happened in the past. They have stayed away. We must face the fact that large numbers of highly-trained chemists decline to present themselves for our examinations." And later he says. "The fact is that the qualifications of many of them are quite up to the level of those which we demand of candidates for the Associateship." Meanwhile there can be no doubt that the Institute has done and is doing much to raise the status of chemists.

The British Association of Chemists—your own Association—also seeks to elevate the profession, if I understand rightly, in a somewhat similar manner to the Institute of Chemistry, but without holding examinations; some of you also, aiming at making the practice of analytical and industrial chemistry a close profession, and in addition to this to some extent employing trades union principles for increasing the payment of, and obtaining certain privileges for, your members.

The National Association of Industrial Chemists, I understand, makes still more distinctive use of these principles, regarding them as one of the most effective means of securing the welfare of the chemist, as interpreted by higher payment

Reverting to the question of improving the status of chemists generally; we know there are two main methods which can be employed to bring this about, namely, technical and moral.

*Technical.*—(1) By rendering the chemist really more efficient and valuable, *e.g.*, by making his analyses of a regularly higher standard and degree of accuracy, and teaching him to apply his knowledge of chemistry, and the other characteristics of his training, to practical purposes.

*Moral.*—(2) By propaganda. (*a*) Demonstrating to and impressing upon people that he really is very valuable. (*b*) Implying or *asserting* that this is so, and as regards the members of certain societies, showing *as proof* of this, that they have passed certain examinations, obtained certain University degrees, or are possessed of certain qualifications considered equivalent. (3) By combination, &c., to force those employing chemists to pay them more

As you will have seen from the brief description of the outstanding features of the societies, they seek to improve the chemist's status *technically* by making him study, and examining him, and *morally* by seeking to give him more *amour propre*, by propaganda, by using trades union principles for securing him better pay, and by the automatic exclusion of all who do not conform to their standard.

Now, whilst some of us may not approve of all the methods employed by these Societies, we must not forget that each of them is attacking part of the problem, and we should not criticise them severely on that account, or simply because the scheme does not cover the whole ground. Each society no doubt follows the course it thinks for the best, and I should like to see all taking a broader view and aiming rather less at benefiting their own members exclusively, and trying still more to advance Science, and to improve and elevate the profession as a *whole*. The greater the status which any society wishes its members to hold, the more important is it that it should be conducted on high principles. Further, if they were all pulling together and working in concert for a common aim, more advance would be made. As it is, there is some overlapping and some gaps occur. A good deal has, however, already been done towards this, such, for instance, as the preparation of Abstracts by the Chemical Society and Society of Chemical Industry in conjunction.

I have sometimes been asked: "If I join such and such a society will it do me any good?" So far as a works' chemist is concerned, frankly I do not think that his being a member of some Society or being able to put certain letters after his name will have much effect in the matter of pay with most managers; at any rate, it is no use depending on it. The benefit is largely reflex, in making him try to be worthy of its traditions, attend its meetings, follow the papers and discussions, study its proceedings, and especially himself preparing a paper for it. In short, he gets most who gives most.

Now it is well known that if we would improve anything we must lay bare its weaknesses and

*An address given to the Glasgow Branch of the British Association of Chemists, October 19, 1921.

study how they may be removed, and this applies equally to the chemist.

As regards technical matters, I have long felt that there was nothing which had such a prejudicial effect on the status accorded to chemists by laymen as the occasional disagreements between their analytical results.

In fact, you will meet people from time to time who will tell you "chemists are no good," and proceed to quote some glaring example of two chemists of standing finding distinctly different results. And although most of the serious differences if investigated prove to be due to variations in sample, yet we know some methods are far from perfect, and that there is sufficient ground for complaint from the commercial man's point of view to make it imperative for the chemist to look into this matter and use every means for improvement.

As far back as 1894, Mr. E. Windsor Richards thought this matter of such importance as to bring it before the Iron and Steel Institute in his Presidential address, and said: "Very considerable trouble and expense have been experienced by manufacturers through differences in analysis by different chemists." Later, before the same Institute, in a paper by my son and myself, we referred to this and pointed out that figures specified should not have uncertain values, and that a figure such as, say, 0·07 per cent phosphorus depended entirely on the personality of the reference chemist; if he found a high result this might limit the steel maker actually to 0·055 per cent, or, on the other hand, allow him up to 0·08 per cent.

This state of things gives rise to distrust, and undervaluation of the ability of the chemist. The layman does not know the limits of usual accuracy of methods, and particularly of methods worked hurriedly. Thus, whilst on the one hand he presses the works chemist for the utmost speed, he blames him as unreliable if the reference chemist's result turns out differently.

For, in such cases it is generally the works' chemist who is believed to be wrong. Many years ago this fact was brought home to me, and I, like many others, felt it deeply.

I have often, during my career as a works' chemist, felt the singular appropriateness of Rudyard Kipling's lines:—

> "The Toad beneath the harrow knows
> Exactly where each point prick goes
> The Butterfly upon the Road
> Preaches contentment to the Toad"

You can guess who the butterfly is.

Hence regular agreement between chemists on what purports to be the same sample is a *sine quâ non* if as a body their status is to be upheld.

Next to the limits of accuracy of methods, the greatest obstacle to regular agreement is professional pride. You know the old saying, "doctors differ," and how No. 2 smiles when you tell him what No. 1 said, and conveys the feeling, "what else could you expect if you went to him?"

There is a good deal of this about chemists too; not only chemists in private practice, but in some works' chemists also, and people of this turn of mind adopt the attitude: "The methods I have selected, and the way I work them give right results, and I don't propose submitting them to any test which might show, or appear to show them to be wrong."

I understand that one well-known institution used for reference refuses, in cases of differences, either to let chemists work side by side with them, or to return part of the samples

In such circumstances, therefore, the works' chemist, though he may feel convinced he is right, is, or was until recently, in a hopeless and very uncomfortable position.

As early as 1886, I felt this strongly, and commenced to write a paper entitled "Works' Chemists and Analyses," dealing with the subject. I never finished it because I realised our hands were tied. What we needed was some means which could be used in any particular case to *prove* who was right, and until we had that, merely to assert that we were right would be futile. From that day to this my interest in the works' chemist and his difficulties never weakened, but became stronger.

I may perhaps be permitted briefly to refer to two ways in which during the last few years endeavour has been made to meet these difficulties.

The first has in view particularly, enabling hard-driven junior assistants who have to make certain tests of the same kind, time after time, to do this easily with accuracy and more quickly. By standardising the methods in question, making their chemical principles clear, and ensuring their exact observance, variable factors and drudgery are largely removed, and the assistants have a better opportunity to improve their knowledge both of those and of further methods.

This system, and also some of the methods, have been described in various papers, one of them by your fellow-citizen, Mr. Herdsman.

The second had for its object proving who was right in case of disputes by affording some means for gauging the accuracy of the work of the analysts who differed. I am sure you all understand that if in such a case, for instance, a sample of unknown composition is run through side by side with a uniform sample the composition of which is accurately known, and the latter gives the correct result, then the probability that there is any error in the testing of the unknown is very small.

If a representative selection of makers, users, and independent chemists have jointly standardised these samples, and will on this account, and because of their wide acceptance and use, acknowledge them, the rest is simple.

This is just what has taken place owing to the co-operation of a large number of such chemists, and to-day there is a range of plain carbon and alloy steels and cast iron, comprising 78 standardised results for elements, available and in use in the British Isles and other countries; this type of method used for determining each element, and the result found by each co-operator who has tested it, being shown in a certificate issued with it.

But apart from technical improvement there are other ways in which chemists can improve their status. They must, of course, have sufficient chemical knowledge to fill their own position—and preferably a good deal more—but that alone is not sufficient. Every manager knows there are qualities of greater value than the purely technical knowledge of one's own business. We have had many examples, especially of recent years,

of men being offered controlling interests in businesses of which they had little or no technical knowledge—and proving successful too—simply because they had organising ability, or some other quality which outweighed what they lacked.

The same principle applies to lesser things, and conversely a young chemist who has considerable technical ability may neutralise the value of this in his employer's eyes by some fault or deficiency of a quite ordinary nature. Let us follow this thought for a moment.

You all know that an analysis which is not accurate is worse than none, because it is misleading; it purports to give certain information, and that information is incorrect. And accuracy depends on carrying out the method which is capable of giving correct results with absolute precision in every detail.

To the chemist the two most valuable assets—essentials in fact—are precision and integrity. The first demands the second. Precision is integrity in little detail. Apart from our recent labour troubles, one thing our industries, and indeed, progress generally, are suffering from, is want of precision You can trace it in almost everything. For economy and progress in manufacture we need a closer approach to the conditions of the laboratory; finer working and greater regularity all through.

In an address to the Cleveland Institution of Engineers, 1907, I traced how this hindered the iron and steel industry. and have repeatedly referred to the same facts in discussion. In short, the national, and indeed world-wide canker, the spirit of the age, is a revolt against precision and painstaking in all the so-called little things of life.

Now the reason I venture to mention this point to you is, that no class of men better understands the truth of what I say than chemists, and it is easy to see how useful the chemist can be to manufacture, when permitted to control it, not for his chemistry alone, but by his influence, the introduction into it of precision, orderly and systematic working, and exactitude in detail.

Indeed, this influence may extend for beyond manufacture, and imbue the world around him with the same spirit. It is largely through the example and influence of chemists that we may hope to counteract the plausible, and on that account all the more injurious tendency which—as many thinking men realise—has spread during the last generation through almost all circles, viz., the tendency to lax and slovenly ways, inattention, and forgetfulness. The war unfortunately gave a certain amount of excuse for general slackness, and the public were not slow to avail themselves of it to the full.

Those who try to fight it down are generally regarded as being unreasonable, and expecting too much: "anybody may forget," they say"; "you can't expect old heads on young shoulders," and so on.

People can understand the seriousness of the slightest laxity when it is a question of giving the wrong tablet on a single line railway, or smuggling matches into a fiery mine or explosive factory. Yet the same holds good for nearly everything in life, and is fatal to many young people's progress.

Laxity is really a form of selfishness, for he who yields to it, in order to save himself an infinitesimal amount of trouble, may cause a disproportionate amount to fall on someone else. On similar lines, one department of a works, to save itself a little extra trouble and a few coppers may cause another department to lose several shillings

Arising out of this, it would be well if every chemist who wants to get on—and every employee for that matter—would keep in mind that a manager's time is more valuable than his own, and not a minute of it should be wasted through any fault of his.

The manager's function is largely creative; he has to think out schemes for progress of the concern. Continual little wastes of his time, whether through technical matters or such things as I have named, effectively hinder him. Naturally, therefore, he values those most who use forethought and attention, and on whom he can rely.

Anyone who has studied the run of an express train (such as is sometimes given in *The Engineer*) will be struck by the serious reduction on the "all-over" speed per hour of a succession of short stoppages, and how these mount up.

Why do so many who give addresses drift into similar non-technical questions? Simply because they who give them realise the important bearing which these have, not only on our industrial life, but our general well-being.

Let us now look very briefly at several successive stages of a chemist's career, and how he may seek throughout it to improve his status. I need say very little as to what is desirable as regards the purely chemical part of it, as this for each branch will be shown him by his chief. If he is able to enter the profession with the training and along the lines recommended by the Institute of Chemistry, this will have been well looked after. If he has not had these opportunities, but, as so many young men have done, has gone straight into a *works' laboratory* with only an ordinary school training, obviously he must try all the harder by attending technical classes, and studying some of the excellent text-books, of which there are so many, to make good his deficiency. But he must *not* rely on the chief chemist to teach him general chemistry, for this hard-worked official usually has far too many duties for him to be able to do more than instruct him as to the matters of the particular laboratory, and at most give him, if applied to, some general indications and advice. But whatever the beginner's chemical education, and the steps he has taken to improve it, there are many things he can do to improve himself and make himself valued.

He should keep always before him that he has entered a *profession,* and by intelligent and conscientious work try to live up to the dignity of it I have already referred to the advantage of joining one or more chemical or technical societies, and to the importance of paying very close attention to instructions given him Hence, when receiving them, he should remember that it is *his* business to make sure he understands them correctly, not the employer's to hammer them into him. He should at once make notes of what he is told. He must concentrate first on learning his own work as perfectly as possible. He must also keep his eyes and ears open to learn and understand as much as he can of the processes that are

going on around him. He must get a clear conception exactly for what object any given analysis is made, what information is wanted, what it really shows, and how its significance is to be most clearly conveyed and interpreted to non-chemists. He should also consider what analyses should be made to cast light on some particular works' problem. The more advanced his position, the more necessary these things are. He should study deductive reasoning, but when practising this, be very careful to keep himself unbiassed. He must not try to make facts fit what he wants to prove or he will hoodwink himself. Then, when he has done this, he should try and be an understudy to the man above him.

As he becomes more experienced he should try to look at these things as though he were in the chief chemist's place, and think what course he would take if it devolved on him to carry out the work and investigations.

If he reads collateral technical literature, such for instance as metallurgical and engineering newspapers, it helps to broaden his mind, and show him some of the problems and points of view of other workers.

The chief chemist in turn should mentally put himself in the works' or general manager's place, and ask himself what he would do if he were really in that position? Perhaps when he comes to think it out seriously, he finds he has not got quite so many easy solutions to the various problems as he may have thought when he was simply criticising their action.

To do as I have indicated tends to increase the sympathy and appreciation of each man for the one above him, and enables him to give more willing and effective service.

So too, if he is aiming at commencing a public practice of his own, he must picture himself in that position, where he has to stand alone far more than in a works, and where he cannot afford to make mistakes at all.

For, the chemist in public practice depends entirely on his *reputation*, which means that there is expected of him practical infallibility in analysis. Hence, any carelessness in him or his staff, if not detected, would be fatal. I need not, however, say more about him beyond this, as he is outside the scope of my remarks.

As regards the works chemist, my own feeling is that the works' laboratory is the finest possible field for a voluntary hard worker, and since the test in real life is not what a man knows but what he achieves, as a training ground it develops ability and resource to an extent which academical training alone cannot, the very difficulties bringing out a man's better qualities.

I should like to see this taken more into account by those who from time to time attempt to gauge a works' chemist's fitness for admission to some society, or in any way confer honours, and with whom at present the qualifications of theoretical knowledge still appear to weigh most.

Now I wonder whether I dare say anything to you on so delicate a subject as the use of combination and trades union principles or methods by works chemists for improvement of their financial status?

If I understand rightly, your Association has—reluctantly and through the inelasticity of the law—as a matter of form registered as a trades union for special reasons apart from the general principles, and the majority of you do not wish to follow these.

I know, however, that the idea does rather appeal to many young chemists in works who see other youths, who do considerably less skilled work, earning more money. That is why I will venture to submit one or two thoughts on it for your consideration.

I mentioned earlier, that the balance and correct sense of proportion acquired from the nature of their business enabled chemists to deal safely with forces otherwise dangerous. So, combination used as a weapon to enforce some concession needs to be employed with great care; and with knowledge and realisation of its full effects, direct and reflex, or it may defeat the object for which it was employed, or have disastrous effects in an unlooked-for direction.

It would appear that your Association is handling it with great care, but many workers have experienced its dangerous side, and I fancy ideas will be modified a good deal in the near future.

Chemists, as some of the principal thinkers of the world, should be *leaders*, not *led*, and although I certainly want to see chemists more highly valued and better paid, I doubt whether this method is so suited to their case, and though it may succeed as regards payment, especially for juniors, it will be harmful in other respects

It seems to me rather an admission of a weak position and of individual inability to rise above the average. Then, any sort of standard payment (such as combination secures for a class), always depends on *averaging*, which for many individuals means levelling *down*, rather than levelling up.

The wholesale regulation of wages may be desirable for *masses* of relatively uneducated men doing work of a uniform and comparatively low mechanical type, but the chemist should be doing work which constantly requires more and more ability. Hence he particularly should not be bound by anything that checks the advancement of the individual, as he improves.

But the greatest objection to this use of combination is, to my mind, that its results are usually directly contrary to the spirit which animates the true chemist, namely, the pride in good work, which it is so desirable should spread through the world, and towards which his example and influence is so much needed.

In the early stages there was the pride of the craftsman, each man striving to excel in his own vocation. Now the whole tendency seems to be to hinder men from doing better work than their fellows, and to grind them down to a common level.

By all means strive to improve your financial position and material welfare, but do not adopt methods which will react to your disadvantage In your effort for this, depend chiefly on the making of yourselves better, more able, and of such worth that men *must* have your services; and get the satisfaction of your increasing capability, and in the feeling that you have done good work.

Perhaps you think I am saying far too much about the moral aspect. I have done so because I believe that it is chiefly the moral qualities

which bring a man success and give him happiness, and it is these alone which will bring about a better state of things in the world between employer and employee, and in all the relations of life. Can any of you tell me of a better or more powerful means?

I have used the word "moral" in its widest sense, but I think you will agree that what may really be called moral qualities in the secular sense, such as diligence, perseverance, &c., are the outcome of the deeper, more spiritual quality. I have already referred to the fact that the necessity of recognising these things as vital factors in business affairs is being acknowledged more and more of late by hard-headed practical men, and want to read you a few words, *not* out of a parish magazine by a clergyman, but out of a very able paper before the Royal Society of Arts, which you will find in the *I. & C. Trades Review* (February 28, 1919, p. 263), by the Chairman of Messrs. Cammell Laird's, Mr. W. L. Hichens, on "The Wage Problem in Industry." In concluding, he says: "Ultimately all industrial questions as well as all other questions affecting human relations resolve themselves into moral problems, and how far we succeed in solving these questions depends on the degree of moral consciousness . . . The words 'Seek ye first the Kingdom of God, and all these things shall be added unto you,' have become a commonplace of literature, and are probably endorsed in church on Sundays by innumerable congregations as sound doctrine, but inapplicable to the affairs of every day business." Once back in the workaday world, common sense prompts us to murmur:—

"Ah, take the cash and let the credit go,
Nor heed the rumble of the distant drum ...."

But is it really common sense?

The Presidential address to the Economics Section (F) of the British Association given by the same author and published in the September 16, 1921, number of the same journal, pp. 395-6, also very ably deals with the same problem.

Unless men with the knowledge and balance of chemists will believe and act on these principles in their lives, how can we expect workmen or others to do it?

Until the employee, and in fact, every one who has a commodity to sell, whether it be goods, brains, or manual labour, learns that his self-esteem demands that he should be as much concerned to *give* good value as to *receive* it, we shall never have a really satisfactory state of affairs.

I feel sure you will have gathered from what I have said that both for happiness and for success in business one must have the driving force of a definite ideal

A man may be a good chemist technically, and yet not achieve much for want of this.

On the other hand, there are men who show no moral aspirations, and will tread on anyone's shoulders to get on rapidly. They don't get on *because* of their objectionable qualities, but in spite of them, because they have an ideal, albeit a low one, and are always working towards it. Hence, though they show no concern for others, they study their employers, anticipate their wishes, and make themselves as useful as they can to them.

Now a few final words, especially to the younger men. Don't waste time thinking over the injustices you have suffered. Everyone suffers lots of injustice and hindrances in their attempt to get on. If blamed, consider carefully whether there is not really some justification. Then you will extract any good there is to be got out of it.

Don't exaggerate the idea of your own value, but make sure that you really are valuable.

Don't be discouraged if success seems a long time coming.

Fix on a strong, clearly defined ideal, and "think high" If your ideal is low you will achieve a low standard. Then *have confidence* in yourself, and don't be afraid to follow wherever it leads you.

You will then probably find your present position offers, or can be made to offer, wider opportunities of advancement. If you are quite sure you can't achieve it in that position, then leave it, and if you really have the value you think, you are bound to get a better—you can't sink.

I cannot do better than conclude with two verses from Ella Wheeler Wilcox's "Limitless":

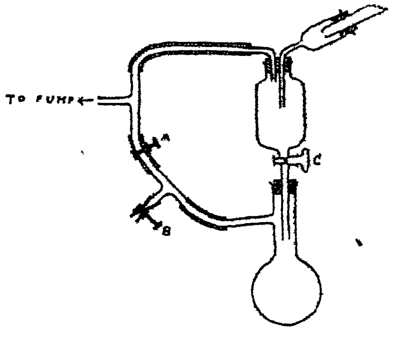
"When the motive is right and the will is strong
There *are* no limits to human power,
For that great force back of us moves along
And takes us with it in trial's hour.

"And whatever the height you yearn to climb,
Though it never was trod by the foot of man,
And no matter how steep—I say you *CAN*,
If you will be patient--and use your time"

## A SIMPLE RECEIVER FOR FRACTIONAL DISTILLATION UNDER DIMINISHED PRESSURE.

By E. J. WILLIAMS

THE subjoined sketch illustrates a receiver, working on the principle of that of Lothar Meyer, for fractional distillation under reduced pressure. The receiver of Lothar Meyer has not hitherto been manufactured by any English firm. It is rather a fragile piece of apparatus, and the form at present exported from Germany (with a ground glass joint) requires firm handling whilst changing the receiver.




The form illustrated can readily be constructed in the laboratory. A small wide-necked tap-funnel is fitted with a two-holed stopper. Through one hole passes an adapter into which the condenser tube leads. A tube through the other hole is connected with a T-piece, one arm of which leads to the manometer and pump. The receiver proper is a small distillation flask to whose side

tube is connected a second T-piece joined up as sketched, A and B being screw-clips.

To change the receiver C and A are closed, then B is opened, when the small distillation flask may be disconnected and replaced by another without interrupting distillation. B is then closed and A opened followed by C.

The clips A and B, with their connecting T-piece, may, of course, be replaced by a three-way tap, which may be made in one with the upper T-piece.

Royal Grammar School,
Newcastle-on-Tyne.

## THE AIMS AND BOUNDARIES OF PHYSIOLOGY.*

By Sir WALTER M. FLETCHER, K.B.E., M.D. Sc.D, F.R.S.

Upon the occasion of our meeting in this metropolitan city of Edinburgh, the seat of an ancient university and a great centre of medical study and practice, it has occurred to me that it may be profitable for us to consider the part which physiology should rightly take in its relation to national life, to learning, and to medicine. Not only the place of our meeting, indeed, but some special circumstances of the present time seem to make it fitting that we should here review the progress, the proper scope, and the prospects of our chosen subject. We are now just half-a-century from the time when physiology first came to take its present position in this kingdom as one of the great branches of university learning and as a vital branch of medical education. We have seen the close of a war which, though it diverted and distorted the progress of the science, yet brought it great opportunities of service in national life and taught us lessons, here as in so many other directions, of which we shall do well to take profit. The passing of the War, moreover, has brought a period of change and unrest during which impulses towards reform are being chequered by the results of fatigue or reaction. Both here and in America it may be said that, while physiology has come from the war with enlarged outlook and responsibilities, it is exposed to some new and perhaps dangerous influences in the present time of rapid resettlement. It may be worth while, then, to look now both forward and back, to see the road by which we have hitherto been led and its relations to that which now lies before us.

I.

Physiology, as the passing generation has known it, took shape and established its boundaries in this country just fifty years ago, when, shaking off its long subordination to anatomy, it was brought to a new life of recognition and progress. The seventeenth century had seen England famous for her schools of physiologists, leading the rest of the Continent in experimental results and in new ideas. Working upon the foundations laid by Harvey, that brilliant group at Oxford—Boyle, Lower, Mayow, Willis—had brought new light to the study of the living body. Nor was their service only recognised by fellow-workers abroad or by those that came after. Their names and fame were on fashionable lips; like that of their predecessor Harvey himself, under Charles I., and of that other Cambridge philosopher Glisson, their immediate contemporary, their work was aided by the direct interest and favour of the sovereign. But, during the eighteenth century and the earlier part of the nineteenth, eclipse fell upon the light that had thus burned so brightly, though isolated gleams shone here and there. James Jurin, under George II., applied the Newtonian principles to calculating the work done by the heart and to other problems of the body, but his efforts to lay true and exact foundations for the study of disease were premature in the absence of experimental data. Stephen Hales, Chaplain to the future George III., made the first measurements of blood pressure in his garden at Teddington, and made many far-reaching observations of the first importance; but, as he wrote, there was indeed "abundant room for many heads and hands to be employed in the work, for the wonderful and secret operations of Nature are so involved and intricate, so far out of the reach of our senses . . ."; and it was not then or till much later that many heads and hands were ready to be employed. Neither of these men had effective influence upon the thought or practical affairs of their day, either within the universities or outside them.

Physiology, as we know it now in this country, took its shape in a new revival which may be reckoned as beginning half-a-century ago. All our chief schools may be said to derive their lineage from that new home of active and unshackled inquiry—I mean University College, in Gower Street, London—and from the influence there of an Edinburgh graduate, William Sharpey, who at the age of thirty-four was taken from the Edinburgh school to be Professor of Anatomy and Physiology. Here, from 1836 until 1874, Sharpey was inspiring a group of younger minds with his eager outlook. Already in France the new experimental study of the living functions was being established by Claude Bernard—that true "father in our common science," as Foster later called him; already in Leipzig Ludwig, transmitting the impulse of Müller's earlier labours, had founded that school of physiology which moulded the development of the subject in Germany and other countries, and had very strong early influence upon several of those who were later to become leaders with us. England had lost the pre-eminence that Stuart kings at all events had valued and promoted. Learning had become identified in English society with the mimetic use of the dead languages, and progress at the two universities—even at the Cambridge of Newton, where mathematics kept independence of thought alive—was still impeded by the grip of ecclesiastical tradition and by sectarian privilege. But at University College learning had been unfettered. Here Sharpey and his colleagues were in touch with the best progress in France and Germany, and here the organised study of physiology as a true branch of university study may be said to have begun. Its formal separation from anatomy came later and irregularly; a separate Chair of Physiology was not created at University College until 1874, nor at Cambridge or at Oxford until 1883.

We ought in piety to recognise that this tardy reflection of Continental progress in our own sub-

* Address delivered before Section I, British Association (Edinburgh Meeting).

ject, like parallel movements in other subjects, had in its early stages received invaluable aid from the Prince Consort, who, familiar with the progress of other countries, had lent his influence and sympathy to many men of science in their struggle against the insularity and apathy of the wealthy and governing classes of the earlier Victorian days. The curious may take note that the first outward mark of recognition given by the official and influential world to the existence of physiology as such was given not, as in other and poorer countries much earlier, by the endowment of some chair or institute for research and teaching, but by an act of symbolic representation. For, when the expensive statuary of the Albert Memorial was completed in 1871, it was found that "Physiology," betokened by a female figure with a microscope, had been given its place among the primary divisions of learning and investigation acknowledged in that monument to the Prince.

From Sharpey himself and his personal influence we may trace directly onwards the development of all the chief British schools of physiology whose achievements have in the past half-century restored Britain to more than her old pride of place in this form of service to mankind. We here fittingly acknowledge first the close link with Sharpey which we find here to-day in Sir Edward Sharpey Schafer, who, after fruitful years in his old teacher's place at University College, brought that personal tradition back to this great school of Edinburgh from whence it originally came. At University College itself the line has been continued with undimmed lustre by Starling and Bayliss and their colleagues to the present day. From Sharpey's school again are derived the great branches which have sprung from it, both at Oxford and at Cambridge Burdon Sanderson, Sharpey's immediate successor at University College, proceeded thence to Oxford and founded there, against many difficulties of prejudice and custom, the school of physiology which Gotch, Haldane, and Sherrington have nevertheless maintained so brilliantly in succeeding years. To Cambridge, Michael Foster, one of Sharpey's demonstrators, was invited in 1870 by Trinity College to be Praelector in Physiology and Fellow of the College. This enlightened and then almost unprecedented act, no less than the personal qualities of Foster that so aboundingly justified it, I would, as in private duty bound, hold here in special remembrance. Under Foster's influence there came into being at Cambridge a strong and rapidly growing school of physiologists, from Langley, Gaskell, Sherrington, Hopkins, to numerous successors. There sprang from him, too, a new impetus to other subjects, through his pupils Francis Balfour and Adam Sedgwick to embryology and zoology, through Vines and Francis Darwin to botany, through Roy to pathology. From Foster again through Newell Martin, who, coming with him from London, had caught not only inspiration from him but some of his power of inspiring others, and who left Cambridge for a Chair at Baltimore in 1876, we may derive a large part of the growth and direction of physiology since that time in the United States and in Canada. The rapid progress of all these biological sciences at Cambridge within a single generation, and the volume of original work poured forth depended, of course, upon two necessary conditions. The first is one which has never failed in this country —the existence of men fitted by temperament to advance knowledge by experiment. The second has been the supply of living necessities through the ancient endowments of the colleges, and these in the Cambridge of the last half-century have been freely and increasingly used in catholic spirit for the increase of any of the borders of knowledge.

If these have been the chief lines of descent along which our present heritage has come to us, as mind has influenced mind and the light has been passed from hand to hand, what has been the outcome as we look back over the half-century to those small beginnings?

Truly we can say that the workers in this country have in that short space of years laid the whole world under a heavy debt. In whatever direction we look we seem to see that in nearly all the great primary fields of physiological knowledge the root ideas from which further growth is now springing are in great part British in origin, and based upon the work of British experimenters. If we consider the blood circulation we find that our essential ideas of the nature of the heart-beat were established by Gaskell, and that other first principles of its dynamics and of its regulation have been laid down by successors to him still with us; that the intricate nervous regulation of the arterial system has had its chief analyses here, and that here have been made more recently the first demonstrations of the part played by the minute capillary vessels in the regulation of the distribution and composition of the blood. Of the central nervous system the modern conceptions of function in terms of the purposive integration of diverse impulses along determined paths have sprung direct from British work, while the elementary analysis of the structure and functions of the sympathetic nervous systems has been almost wholly British in idea and detail. As with the nervous regulation of the body, so with the chemical regulation of function by travelling substances—the so-called "hormones," or stimulants from organ to organ—this, too, is a British conception enriched by numerous examples drawn from experimental work in this country. In the study of nutrition, of the primary "foodstuffs," proteins, carbohydrates, fats, salts, and water, whose names in their supposedly secure sufficiency were written with his own hand by Foster upon the blackboard shown in his portrait by Mr. John Collier, to typify, as we may imagine, a basal physiological truth, we have come to learn that these alone are not sufficient for growth and life in the absence of minimal amounts of accessory unknown and unstable substances, the so-called "vitamins," which are derived from pre-existent living matter. This conception, undreamt of to the end of the nineteenth century, has fundamental value in medicine and in agriculture, and has already begun to bear a harvest of practical fruit of which the end cannot be seen or the beneficence measured. This discovery stands to our national credit, and large parts of its development and application have been due to recent British work. If we turn to the regulation of

respiration and its close adaptation to body needs, that also, as it is now known to the world, is known as British labours have revealed it, just as the finer analyses of the exchanges of gas between the air and the blood and between the blood and the body substance have been made with us. The actual modes by which oxygen is used by the tissues of the body, its special relations to muscular contraction, the chemical results of that contraction, the thermal laws which it obeys—all these fundamental problems of living matter have seen the most significant steps to their solution taken within the past generation in this country.

Work of this kind brings permanent enrichment to the intellectual life of mankind by giving new and fuller conceptions to the nature of the living organism. That we may think is its highest function; but it does more than this. Just as all gains in the knowledge of Nature bring increase of power, so these discoveries of the past fifty years have their place in the fixed foundations upon which alone the science and the arts of medicine now or in the future can be securely based. The special study of disease, its cure and prevention, has had notable triumphs here and elsewhere in the same half-century, and these as they come make as a rule a more spectacular appeal to the onlooker. Yet it is the accumulating knowledge of the basal laws of life and of the living organism to which alone we can look for the sure establishment either of the study of disease or of the applied sciences of medicine. As we have seen, there are few indeed among the fields of inquiry in the whole range of physiology in which the British contributions to the common stock of ascertained knowledge or of fertile idea do not take a foremost place. It would be impiety not to honour, as it would be stupidity to ignore, these plain facts, which, indeed, are now perhaps more commonly admitted abroad than recognised at home. There is no occasion here for any spirit of national complacency—rather the reverse, indeed. British workers at no time earlier than the War have had the menial assistance or other resources which their colleagues in other countries have commonly commanded, and too often the secondary and relatively easy developments of pioneer work done in this country have fallen to well-equipped and well-served workers elsewhere. If in the past half-century better support had been available from public or private sources, or at the older universities from college endowments, it is impossible for any well-informed person to doubt that a more extended, if not a more diversified, harvest would have been won.

We stand too near to this remarkable epoch of progress to appraise it fairly. In the same span of years Nature has yielded many fresh secrets in the physical world under cross-examination by new devices which have themselves been lately won by patient waiting upon her. So great a revelation of physical truth has been lately made in this country, bringing conceptions of space and of matter so swiftly changing and extending, that our eyes are easily dimmed to the wonders of that other new world being unfolded to us in the exploration of the living organism. Only the lapse of time can resolve the true values of this or that direction of inquiry, if indeed there be any true calculus of "value" here at all. We seem to see in the progress of physiology, not at few but at many points, that we stand upon new paths just opening before us, which must certainly—as it seems—lead quickly to new light, to fuller vision, and to other paths beyond The advances of the next half-century to come must far exceed and outshine those due to the efforts of the half-century just closing; that is probably the personal conviction of us all. Yet we may still believe that through all the history of mankind recognition will be given and honour be paid to the steps in knowledge which were made first and made securely in the period we now review. The men who have done this work will not take pride in it for themselves; they know that their strength has not been their own, but that of the beauty which attracted them, and of the discipline which they obeyed. They count themselves happy to have found their favoured path. Other and more acute minds might have usurped their places and found greater happiness for themselves if, under a social ordering of another kind, they had been turned to the increase of knowledge instead of to the ephemeral, barren, or insoluble problems of convention and competition. By how much the realised progress towards truth and the power brought by truth might have been increased under a changed social organisation we can never know, nor can we guess what acceleration the future may bring to it if more of the best minds are set free within the State for work of this highest kind, what riches may be added to intellectual life, or what fuller service may be given to the practical affairs of man and to the merciful work of medicine.

II.

To the story of progress which has just been sketched in outline the War brought inevitable interruption and change. To the more obvious disturbances and wastage of war I need not here refer, but I would point to some influences of that time which will be found, I think, to have left permanent effects, and on the whole good effects, upon the position and tendencies of physiology. Before 1914 physiology was being developed, as we have seen, in its still youthful status as one of the primary departments of knowledge; it had become a subject of independent university rank Large and important parts of this development had proceeded at one or other of the ancient universities, out of touch with great centres of population, and out of touch, therefore, with immediate medical needs. In some degree this was not without advantage, and for two main reasons Detachment from the pressure of need allowed the free pursuit of knowledge for its own sake and a full surrender to the hintings of Nature, wherever her clues might lead the inquirer. Experience amply showed, moreover, that when physiology was presented among other university subjects for study it gained, first as recruits and later as distinguished workers, many able young men who were attracted to it, often from other subjects, by the fascinations of its problems, and without regard to any of its potential applications to medical or any other practical ends. These were great gains which it would be easy, if it were not unnecessary, to illustrate by many convincing examples. Yet there were some heavy counterweights on the other side of the balance. The practical and urgent needs of humanity as found

at the hospitals were not brought with full or due effect to the notice of physiologists. Those in charge of hospital patients were not selected to advance, or habitually engaged in advancing, medical knowledge, and new physiological conceptions as they took shape in our laboratories only slowly and partially came to have effect in medical practice and medical study. The physiologist, to his own certain loss and to the no less certain loss of medicine, held aloof from the bedside, often when access was possible, and remained immersed in his laboratory interests. Little pressure, indeed, was ever brought to bear upon him by the physician to come to his aid. Connected with the evils of this separation was the divorce which the accidents of development had set up between physiology and pathology, as though the study of the damaged body could be separated from the science of the living organism and of its reactions to any disturbance from the normal. Yet, while the physician had come to tolerate the approach of the pathologist to the bedside, it occurred too rarely that he felt the need of the physiologist, or made himself familiar with new devices of physiological investigation.

If from a hospital in time of peace the most obvious call had seemed in the past to come from the side of infective disease or morbid process for the help of the pathologist, in war the stresses put upon the healthy human body made the physiologist and his methods indispensable Bacteriological work and studies of immunity had their prominent place, of course, in the detection and prevention of infective disease, and wonderful were many of the achievements seen under this head. But in a sense the more complete the prevention of infective disease the more apparent became the physical stresses of war. The violences offered in modern warfare to the human body—whether through exertion and exposure, by terror or excitement, in physical damage by lead or steel or in chemical attacks by poison, and not least through the incredible stress of flying high and fighting in the air—all these brought many new and urgent calls for precise physiological knowledge and for new studies by the physiologist The results of pain and fear, of hæmorrhage, of "shock" by wound or operation—all these needed further analysis before sound treatment could be devised or improved. New studies were needed of changes in blood-pressure and blood-volume and in the qualities of the blood itself, new inquiries into the finer vessels of blood circulation and their relation to the nervous and other systems, and new analyses of the chemical mechanisms of the body and of the modes by which want of oxygen is met by adaptation or leads to final damage. But the well-nigh incredible demands made upon the machinery of man's body in and behind the battle-line, in all situations upon the land or under the earth, high in the upper air, in the sea or within its depths, by no means make up the tale. Our forces were engaged in every climate, from the Equator to the Arctic regions, and were faced by innumerable local or accidental variations of diet. Here again were required the applications of physiological studies of heat loss and of heat production to manifold practical problems of clothing and of diet. What would have seemed a fanciful tale barely 20 years ago might in particular be told of the miracles wrought by the studied application of our new knowledge of "vitamins" in diet, in saving from painful disease or death many thousands of men in diverse climates and fields of war

At home the bodies of the civilian population were exposed to many stresses, often hardly less than those of active service. Men and women alike were exposed to arduous toil, to dangerous occupation, to poisons of many kinds needed for munitions, and in all of these dangers the guidance of the physiologist was needed for the avoidance of industrial fatigue and loss of output and for devising protection against industrial poisoning. The whole nation was threatened by the menace of starvation, and our escape from that, itself one of the governing conditions of our ultimate victory, was due to a system of rationing and of the management of food materials, animal and vegetable, which was based on accurate physiological knowledge, won by experimental methods.

I touch on these points here briefly and in outline only in order to draw attention to the special influence which, I think, the War has exercised upon the position of physiology in this country. The physiologists gave no exceptional help to the nation during the War; the exponents of every branch of science were needed, were ready, and were used, in our national crisis. Hardly one division of science can be named the deficiency of which would not have made defeat inevitable. It is a truism and a commonplace to say that without the help of scientific men and of the fruits of experimental science, though that commonplace has not, I think, ever yet been enshrined in the addresses or thanks of Parliament or in the prayers and thanksgivings of our churches. But we may recognise, perhaps, that the nation as a whole, and those especially who have the government, public or private, of large groups of men in their hands, have learned that obedience to physiological law is a first necessity for the maintenance of the body machinery in health and for its effective and harmonious use. They have come to know, moreover, that the men who alone can guide them to this obedience are those who have learned in the school of investigation from Nature herself. The nation has seen a Minister fall whose control of the people's food was not based on physiological law, and his successor gain renown whose adoption of the teaching of physiological experiment was early and faithful. Nor was this by any means an isolated object-lesson. There is no doubt, surely, that physiologists have a new vista before them of immense public usefulness, if they will hold themselves in readiness to give the same kind of service to the country in the stress of her industrial life during peace as they gave so freely and to such effect in time of war.

But if the War brought these lessons to the general public, what lessons have come from it to the physiologist himself? I would only recall briefly here the considerations which were brought home with sufficient clearness to us all, I think, during and after the closing stages of the struggle. The War, in the first place, displayed before us new and gigantic fields of physiological study. Viewing these so far as we can, even at this distance, dispassionately, we see how the stresses

and accidents of warfare in all their variety offered to our study a series of experiments made upon the human body, and on a gigantic scale. Only by disciplined study of the results at all stages of these trials of war in all their varying degrees of horror and distress could effective aid be given in palliation of suffering or its avoidance It was inevitable that study of this kind and upon so great a scale should result—as, happily, it did result—in much permanent gain to physiological knowledge and to the beneficent power that all sound knowledge brings. New insight was given into the functional patterns of the nervous system and into the orderly hierarchies, so to speak, under which this or that function is brought into subordination to another of superior rank, and new knowledge was gained of the phenomena of separation and repair in the outlying nerve-trunks. Accurate information was collected of the nutritional needs, quantitative and qualitative, of human beings under varying conditions; and in particular, many special conditions of warfare brought to the test, established the fundamental usefulness, and stimulated the growth of that newest chapter in physiology already mentioned—that dealing with the elusive but potent accessory factors in nutrition—the vitamins. These examples must suffice where scores of others familiar to all of you might be given.

In the second place, the experience of the War has had wholesome effect from its tendency to remove the barriers that here and there had grown up between physiologists and the practical needs of medicine. Physiologists had valued, and justly valued, their academic freedom of inquiry within the universities, and indeed, we know that practical utility could not be better served in the long run than by the detached pursuit of knowledge for its own sake. But, partly for reasons of hospital and professional organisation already touched upon, and partly because, to its obvious and immense gain, physiology had attracted from other paths men who were not, and had never become, medical men, there were some capital parts of the subject of which the chief explorers had never used the medical field of work or brought to medicine the weapons they had, unwittingly, at command. We can recognise already that this partial divorce has been changed by the War into a union likely to be increasingly fertile. Of the professorial chairs of medicine or directorships of medical units established since the War, for the advance of medical knowledge within hospitals in accordance with the university standards and ideals acknowledged in other subjects of study, it is remarkable that to the greater number of these there have already been appointed men whose training has been in the methods of physiological laboratory, and who applied that training to urgent medical problems of the War. There is hardly any one of our schools of physiology, moreover, to which some piece of living experience has not been brought in these last years to enforce the old lesson of the value to science itself of bringing natural knowledge to its fullest utilitarian applications. The practical fruits of scientific labour are found, if our hands are put out to gather them, to contain within themselves, like the natural fruits of the earth, the very seeds from which new knowledge and new fertility will spring. Many of our leaders in physiology brought to the problems of war the accumulated knowledge of their lives, as patriotism and humanity dissolved at a touch the hedges of custom and use. I know of not one such who did not find in the application of his vision and training to the actual problems before him, first, a wholesome reminder of the limits of his knowledge and its clarity, and, second, new clues towards its advance, and that by no means only in a familiar or an expected direction. The stimulus of practical need here, as so often in experience, advanced the growth of knowledge beyond the point of immediate application to practice. Those who studied to find the best and most practical means of saving life threatened by severe hæmorrhage, or by the shock of wounds or operation, found in the course of meeting the immediate emergencies almost endless promptings to further enquiries, to be followed then or later—inquiries into the physical, chemical, or biological qualities of the blood, into its relations to the vessel walls, and into the functional changes of the capillary blood system and the factors affecting or controlling them. Those who fixed their attention upon the damage wrought in the respiratory organs by poison gases were led to many new studies of the fundamental physiology of the lungs. The lymphatic system of drainage of the lungs was re-examined, and wide new experimental studies of the modes of regulation of the breathing were undertaken which have thrown new and valuable light upon the normal mechanisms of respiration. An inquiry into the poisonous action of the high-explosive trinitrotoluene, and into the possibility that slightly abnormal forms of this substance, found as a small contamination of the normal form, might be specially toxic, led to a clear negative answer. But it led unexpectedly, it is both curious and useful to note, to the discovery that one of these abnormal forms was an effective reagent in the laboratory. By its means the chemical structure of a constituent of muscle substance known as carnosin was for the first time determined, and carnosin has now been synthesised artificially from simple materials.

In sum, then, we may gratefully recognise that the War in its horror and waste has not brought evil without any admixture at all of good. We may be encouraged at least to hope that the active co-operation which the War established and fostered in diverse ways between the physiologist and the medical or surgical clinician may remain to bring lasting good, on the one side to the cause of learning and its advance, and on the other to medical education and to medical progress.

## III.

If we have looked backward to the development of physiology in the past half-century, and to the influence upon its course which the War has brought about, I would invite you to look forward to the future and to review the aims of physiology and the boundaries to which it should properly extend in its relations to other subjects of study.

Foster, early in his work at Cambridge, spoke of physiology as being the study of the differences between the living body and the dead body. The progress of this study, as it has been carried on during the past generation, may be considered from two directly opposite points of view. Viewed in one way, we may think of this progress as being

a progress in analysis, as a disentanglement of the diverse though not separable functions of the body and of each of its parts. Viewed again, we may see it as a steady progress towards synthesis, towards the unification of all the contributory functions of the parts into a single functional organism.

The analysis of the separate functions of each part of the body was an inevitable mental process as the anatomist revealed more and more accurately the visible machinery of the body. Bichat at the beginning of the nineteenth century had taught that the activities of the body must be the sum of the activities of the organs. The announcement of the universal cellular structure of the organs made by Schwann seemed but to carry this analysis one step further, and to show, that in the sum of the activities of the constituent cells could be found the adequate expression of the functions of the whole body. The rapid improvement of the microscope in the latter half of last century, combined with the new resources of the aniline dyes by which transparent structures could be differentiated and made visible, greatly stimulated the analytic study of the body. As the various glandular structures were made visible, and even, as it almost seemed, the inner life of the gland cell was revealed, as muscle fibres in their different kinds were made plain and the harder elements of the body resolved into the architectures due to different kinds of constructive cell, so it seemed to many that in a little more we should have the quest resolved in an appeal to a congeries of physico-chemical events within the individual cells. Even the mysteries of the central nervous system seemed to be dissolving as the new powers of histology, coupled with refined methods of experiment, showed the intricate pattern of communicating fibre and cell and gave provisional descriptive explanations of many isolated nervous phenomena.

(To be continued).

## NOTE ON THE FORMATION OF HEXACHLORETHANE FROM CHLORPICRINE.

By OSWALD SILBERRAD.

WHEN hydrochloric acid gas is passed through chlorpicrine at 100° C. and the mixed vapour so obtained through a tube filled with pumice and heated to 400° C., the bulk of the chlorpicrine suffers decomposition into phosgene, nitrosylchloride and nitric oxide; a small proportion is, however, converted into hexachlorethane, which may best be collected by passing the cooled gases through a tube lightly packed with asbestos. On extracting the asbestos with a mixture of alcohol and ether, the hexachlorethane was obtained as rhombic tablets which volatilised without melting, but on heating in a sealed tube after resublimation, melted at 189° C., and proved on analysis to be hexachlorethane.

Found Cl=89·2 per cent. $C_2Cl_6$ requires Cl=89·85 per cent.

The Silberrad Research Laboratories,
Buckhurst Hill, Essex.

## NOTE ON NEGATIVE OPTICAL ANOMALIES.

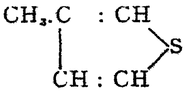
By GERVAISE LE BAS, B.Sc.

THE writer has recently pointed out the prevalence of negative anomalies which affect atoms like bromine, oxygen, and sulphur in organic compounds. These signify a depreciation of the optical refractivity below the normal atomic values as found in saturated compounds.

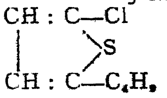
One of the outstanding facts is that the depreciations amount to −0·52, −1·06, and values involving the disappearance of $r_\alpha >O$ (1·48) and $r_\alpha$ : O (2·24).

Among the series of compounds which are affected are furfurane $C_4H_4O$ −0·52, thiophene $C_4H_4S$ −1·10. It has been shown that substituted furfurane compounds like furfural do not show this negative anomaly. The following thiophene derivatives give results from which additional conclusions may be drawn: $CH_2$ 4·60, S 7·96, Cl 5·96, Br 8·79, $r_\alpha$ S 6·86 (lower value).

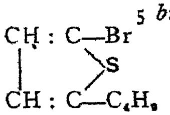
*3 methyl thiophene*

| | $M_\alpha$ | $\Sigma nr_\alpha$ | $\Delta$ |
|---|---|---|---|
|  | 30·06 | 29·80 | +0·26 |

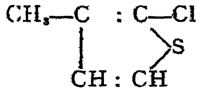
*5 chloro 2 butyl thiophene*

| | | | |
|---|---|---|---|
|  | 48·62 | 48·50 | +0·12 |

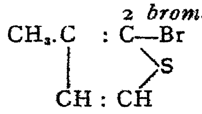
*5 bromo 2 butyl thiophene*

| | | | |
|---|---|---|---|
|  | 51·27 | 51·33 | −0·05 |

*2 chloro 3 methyl thiophene*

| | | | |
|---|---|---|---|
|  | 34·10 | 34·70 | −0·60 |

*2 bromo 3 methyl thiophene*

| | | | |
|---|---|---|---|
|  | 36·86 | 37·53 | −0·67 |

The nett value for sulphur in thiophene is $r_\alpha$ S 7·96−1·10=6·86, is entitled to be regarded as the characteristic one, since it fits in between Cl $r_\alpha$ 5·96 and P 7·77. The atomic refraction of sulphur in the mercaptans, thio ethers, &c., viz · 7·96, would thus show a positive anomaly of +1·10 (8×0·14) *cp*:

$R_\alpha$ $H_2S$ 8·91 $r_\alpha$ S 6·79
$H_3P$ 10·95 $r_\alpha$ P 7·77

(Bleekrode: Jamin's "Cours de Physique" III., p. 36).

The above Table shows that (1) substitution α 2 in position 3 can reduce the negative anomaly to zero. Perhaps positions 1 and 3 are nearer than shown by the formula (central position of

sulphur); (2) substitution on both sides of the sulphur atom practically neutralizes the negative anomaly; (3) the full substitution of one ethenoid group or substitution on one side of the molecule reduces the negative anomaly to half, $-0{\cdot}60$ $(4\times0{\cdot}15)$; (4) Cl, Br, have lost their usual positive anomalies for substitution

CH : CH
| S
CH : CH

It is clearly seen that anomalies analysed as done by the writer in such a way as to distinguish between the two sides of conjugated unsaturated groups is the only one possible. This method of attack appears to make it necessary to recognise electrons as the units which retard the light, and that in some cases they fail to do so. An internal coordination of the electrons or leakage might be responsible. This condition sometimes affects a large number as shown by the disappearance of the atomic refractivity. The electrons of negative atoms seem specially prone to lose their influence, *c.p.*, . CH : N . in pyridine 1 : 1 0·78 only.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

*November* 10, 1921.

Prof. C. S. Sherrington, President, in the Chair.

The following papers were read :—

"*Experimental Researches on Vegetable Assimilation and Respiration. XIV.—Assimilation by Submerged Water Plants in Dilute Solutions of Bicarbonates and of Acids : an improved Bubble-counting Technique.*" By A. J. Wilmott.

By the aid of special apparatus described in the text of the paper it is shown that the increase of "bubble rate" of $CO_2$ liberated from the cut stem of a water plant, found when free acid is added to the water covering the stem, is due to the effect of the acid upon carbonates present. No increase is found when soft water is used.

A comparison has been made in the "bubble rate" in solutions of carbonic acid and of sodium bicarbonate of known strength, and the latter were found to behave generally like solutions of carbonic acid.

"*The Coagulation of Protein by Sunlight.*" By E. G. Young.

"*Optical Rotatory Power of Crystalline Ovalbumin and Serum Albumin.*" By E. G. Young.

"*Longevity of Certain Species of Yeast.*" By A. R. Ling and D. R. Nanji.

Eight cultures of yeast prepared in 1887 by the late Prof. Hansen were found to be still living. In what form they have retained their vitality we have not been able to determine. From the work of Hansen we know that one species at least, *A. apiculatus,* found on the exterior of certain fruits, hibernates in the soil; and as this species, or at all events the yeast with which Hansen worked, does not form endospores, it may be that our yeasts have been preserved as resting cells. Further experiments with these and other species of yeast are in progress.

"*A Quantitative Analysis of the Growth of Helianthus annuus. Part I.—The Respiration of the Plant and of its Parts throughout the Life Cycle.*" By F. Kid, C. West, and G. E. Briggs.

The respiration of the plant was investigated first, to provide data for calculating loss in dry weight of a plant, due to respiration under field conditions, and thus, with data for increase in dry-weight, due chiefly to assimilation, to construct a "balance sheet" for the plant; secondly, to determine effect of age of the plant (internal factor) upon its respiration. Respiration was measured under standard conditions at weekly intervals throughout the life cycle. Standard conditions were—a temp. of 10° C. (at this temperature respiration maintained a constant value for an appreciable time), excess of respirable material (directly after a period of active assimilation), external pressure of oxygen greater than in atmosphere.

The amount of carbon dioxide (mgrms.) per grm. dry-weight per hour produced by the respiring tissue under standard conditions is called the "respiratory index." Consequently the "respiratory index" is a close measure of the "effective amount of respiring cell-matter"—the internal factor involved in respiration. Further, for the first purpose, namely to determine loss in dry-weight due to respiration under field conditions (to be dealt with in later papers), the relation between respiration and temperature (0°-25° C.) was determined.

The "respiratory index" of the whole plant falls continuously throughout the life cycle from 3 to about 0·3. The respiratory index of stem, of individual leaves and of flower decreases with age of the organ. The initial "respiratory index" of successive leaves—*i.e.,* the "respiratory index" of the stem apex—decreases with age of plant, thus indicating that the effective amount of respiring cell-matter per grm. of dry-weight of meristematic tissue decreases with age of plant. Consequently, the fall in "respiratory index" of the whole plant is not due solely to increasing proportion of non-meristematic tissues, such as mechanical and water-conducting tissues.

Fall in the value of the "respiratory index"—rate of respiration per grm. dry-weight—follows closely fall in "relative growth rate," that is, rate of increase in dry-weight per grm dry-weight, thus suggesting some close relation between increase in dry-weight and respiration.

"*The Colouring Matter of Red Roses*" By G. S. Currey.

### MINERALOGICAL SOCIETY.

*November* 1, 1921.

Dr. A. Hutchinson in the Chair

"*The Determination of the Optic Axes of a Crystal from Extinction-angles.*" By Prof. H. Hilton.

The problem of obtaining the positions of the

optic axes of a crystal from the extinction-directions on four known faces was discussed, and it was shown from a purely geometrical standpoint that the solution is unique Their position was also found graphically as the intersection in the gnomonic projection of two cubic curves, on which any number of points can be obtained by the use of the ruler only.

*"Some Minerals from Leadhills."* By W. Campbell Smith.

Caledonite of pale-blue colour and acicular habit have been frequently described in the past as aurichalcite. Examination of all available specimens of so-called aurichalcite from this locality showed that all were caledonite of this acicular habit. The optical properties were found to agree with those of caledonite of the normal habit. It was shown that in caledonite the plane of the optic axes is parallel to (010) and the acute bisectrix is perpendicular to (100) and not as stated in Dana and other text-books. Other remarks referred to gold, linarite, minium, and the rare mineral eosite.

*"An Example of Porphyry-Quartz from the Esterel Mtns. (France) twinned on the face* (1012)." By Dr. J. Drugman

This twin-law in quartz has previously been observed only by Q. Sella in 1858 and has been regarded as doubtful. An example of it has been found amongst the porphyritic crystals in the "blue porphyry" of the Esterel Mtns. A distinction is made between the twins of low-temperature rhombohedral $\alpha$-quartz and those of hexagonal $\beta$-quartz (stable at a temperature above 575° C.).

*"Biographical Notices of Mineralogists recently deceased; with an Index of those previously published in the Mineralogical Magazine."* By Dr L. J. Spencer.

## NOTICES OF BOOKS.

*Applied Colloid Chemistry, General Theory.* By Wilder D. Bancroft. First Edition. International Chemical Series. Pp. 345. New York: McGraw-Hill Book Co. London: 6 and 8, Bouverie Street. Price 18s. net.

The increasing knowledge of colloidal chemistry has been remarkable during the last few years, and the part played by colloidal substances in every branch of chemistry, manufactures, and indeed in everyday life, is becoming recognised.

Professor Bancroft's book is a very valuable contribution to our knowledge of these substances. The author's work as Professor of Physical Chemistry in Cornell University is well known, and he has dealt with the subject in an original and masterly manner.

A large number of references to authorities is given in the text. This method of giving references is of the greatest value to students. It adds much to the usefulness of the work. It is intended that this volume shall be followed by others on such subjects as paints, varnishes, plastics, fibres, dyeing, foods, beverages, &c We await these volumes with interest.

*The Chemistry of Synthetic Drugs.* By Percy May, D.S.C. (Lond.), F.I.C.). Third Edition revised. Pp. xv.+248. London: Longmans, Green & Co. Price 12s. 6d.

We are glad to announce the third edition of this most important work. The author in the preface of his second edition, published in 1918, remarks that before the war the manufacture of synthetic drugs was practically confined to Germany. The unhappy use that that nation made of the knowledge gained by the research in this domain is now a matter of history. The war with all its horrors has shown the unsuspected toxic action of many of these little-known gases. It has shown, for instance, that the material now known as phosgene (carbonyl chloride) is far more toxic to man than prussic acid, and the hitherto almost unknown substance—di-chlorethyl sulphide (familiar to everyone by the name of mustard gas)—has been found to be one of the most dangerous substances known.

During the war and since the armistice, the manufacture of synthetic organic chemicals has been undertaken by British chemists with considerable success, but to enable them to hold their own against competition from a country where factories completely equipped for producing these substances are already in existence, some kind of protection is necessary. Assistance of this kind will probably be obtained in measure, and with the increasing knowledge of their chemistry and experience in their production, there should be nothing to prevent their home manufacture in sufficient quantity to meet all needs.

The value of synthetic drugs in pharmacology cannot be over-rated, but an exhaustive knowledge of their chemical composition and physiological action alone enables them to be produced economically and applied to the greatest advantage.

Dr. May's work is an invaluable contribution to the knowledge of the subject. The work is well printed and indexed, and there is a useful glossary of chemical and medical terms that is of considerable value.

*Inorganic Chemistry.* By E. J. Lewis, M.A. (Cantab.), B.Sc. (Lond.), with Introductory Note by Sir Richard Threlfall, K.B.E., M.A., D.Sc., F.R.S. Pp. xv.+442. Cambridge University Press. Price 9s. net.

In the introductory note Sir Richard Threlfall, while referring to the effort that had to be put forward during the war to put the manufacture of explosives on an adequate basis, called the attention of very many to the important part that chemistry plays in the life of the nation—with the result that a number of young men hastened to take up chemistry as a profession—and his introductory note is specially directed to such. He emphasises the need of a thorough chemical education. "There is always an opening for a good chemist, industrious, clear-headed, logical, and persistent, with a knowledge of the subject wide enough and deep enough to give these faculties full play. There is no room nor prospect for the smatterer."

The book is exceptionally well illustrated, and will be found invaluable to students and to those who propose to adopt chemistry as a profession.

The first part of the book is divided into sections deaing with equivalent mass, the atomic theory and its applications, while Part II. is occupied with the Periodic Law.

Mendeleef's periodic classification and Lothar Meyer's curve showing the relation between atomic volumes and atomic weights are given.

We notice that some of the statements made are open to a certain amount of criticism. For instance, on page 398 it is stated that Crookes in 1878 discovered cathode rays. This is more than Sir W. Crookes himself claimed, for although his researches into radiant matter at that time brought the subject into great prominence, cathode rays had been observed and described some years earlier.

On the same page also it is suggested that Roëntgen in 1895 discovered that when the cathode rays were stopped by a solid target they gave rise to X-rays. It is doubtful whether the true explanation or the true physics of the conversion of cathode rays into X-rays was understood before the introduction of Prof. Jackson's platinum target tube.

*The Electric Furnace.* By J. N. Pring, N.B.E., D.Sc. Pp. ix.+485. London: Longmans, Green & Co. Price 32s. net.

This further valuable addition to monographs on industrial chemistry cannot fail to be of service to those who are working with numerous reactions connected with the very high temperatures. Although a knowledge of the chemical effects that can be produced by electricity dates back to the days of Davy in 1810, it is only in recent years that the electric furnace has become one of the most valuable agents in metallurgical processes. The remarkable researches by the late Henry Moissan in France and the more recent results in London and America have brought home to metallurgists the value of electricity in producing high temperature.

A very complete historical survey of the subject is given in the first chapters, and the various devices that have led up to the present-day methods are fully and clearly illustrated. This is followed by a description of present-day electric furnaces, and the details of the current supply in electric furnace operations.

A good chapter is devoted to measurement of high temperatures and is followed by a description of the methods at present employed for the manufacture of calcium carbide and the synthesis of nitrogenous compounds.

The electric steel processes that have recently played such an important part in the production of high-grade steel are fully dealt with, and most of the systems in present use are fully described and illustrated.

At the end of the book the power expenditure in electric furnace processes in connection with cost is discussed, and statistical information is given of present-day water power and steam-power installations.

A valuable bibliography of books on electric furnaces, ferro-alloys, non-ferrous metals, abrasives, and kindred subjects brings the book to a conclusion.

*Volumetric Analysis for Students of Pharmaceutical and General Chemistry.* By Charles H. Hampshire, B.Sc. (Lond.), F.I.C. Pp. 124, fully illustrated London: J. & A. Churchill. Price 7s. 6d. net.

In this edition of this useful little book some new determinations have been added, and also the section on indicators. The object of the book is twofold—to present a general introductory course of volumetric analysis as well as an additional specialised course for students in pharmacy and analytical chemistry.

The first two chapters deal with the proportion of normal solutions, and then follows a very important chapter on the sources of error in indicators, which is of very great value, as it makes clear many little known reactions that would otherwise cause considerable perplexity to students.

The exercises in acidimetry and alkalimetry that follow are very clearly and simply arranged. The next section of the book deals with oxidation and reduction, and the concluding pages are devoted to miscellaneous exercises.

The book is well indexed and illustrated and will undoubtedly be largely used by workers in volumetric analysis.

*The Chemical Effects of Alpha Particles and Electrons.* By Samuel C. Lind, Ph.D; Physical Chemist, U.S. Bureau of Mines. American Chemical Society, Monograph Series. Pp. 182, illustrated. New York: Chemical Catalogue Co.

This book is the second of the American Chemical Society's series of monographs, and it deals in a systematic manner with what is of necessity an entirely new branch of chemistry. The object of the author of the monograph has been to collect together as much experimental material as possible, and to present it in a form that can readily be followed by those who are unfamiliar with the subject.

Although from the title one would perhaps conclude that the work would be confined to the effect of alpha particles and electrons, the field of photo-chemistry is of necessity introduced. The author acknowledges his indebtedness to the work of Rutherford, Madame Curie, J. J. Thomson, and others.

Chapter I. is devoted to the definition of radiochemistry, and the author explains in some detail what should be comprehended in the term.

Chapter II. gives a brief outline of radioactivity and the properties of some special forms of radium. This is followed by a chapter on ionisation and qualitative radio-chemical effects. The author gives a very brief account of the colouration of glass and minerals by the action of alpha rays. This reaction was very carefully studied by the late Sir William Crookes, particularly the colouration brought about by the action of alpha particles upon diamonds, and by sunlight upon glass.

Chapter VI. deals with the reactions by radium emanation and the experiments of Cameron and Ramsay are fully described and illustrated.

Disintegration by alpha particles is also discussed, and a review is given of the investigations by Rutherford, Darwin, and others, on this im-

portant subject. The final chapter is devoted to artificial radio-activity. The appendix gives useful tables of the decay of radium emanation, and a list of radio-active isotopes. At the end of the book there is a very complete index of subjects, followed by a list of authors quoted The book is thoroughly well printed and illustrated.

## CORRESPONDENCE.

### GRAPHIC REPRESENTATION OF CERTAIN HETEROGENEOUS EQUILIBRIA.

*To the Editor of the Chemical News.*

SIR,—The remarks of Rivett (CHEMICAL NEWS, cxxiii., No. 3213) appear to be somewhat superfluous. In his paper the following phrase occurs: "The phase rule requires variation in the solid phase in binary systems to correspond with variations in the liquid phase." Is not this variation adequately represented by the ordinate A *f a* in his diagram?

In the figure each point denotes a substance of invariant properties. The ordinate A *f a* on the other hand represents the variation in properties of the pure substance A, implicitly if not explicitly.

Obviously, this being true the point A denotes a different substance to the points *f-a*, this variation in properties would include changes in density, electrical conductivity, vapour pressure, and other physical properties.

Would not this variation in physical properties correspond to the excessively minute changes in the solid phase which Rivett holds to be necessary?

From this point of view any substance at say 30° C. is held to be different to the same substance at, we will suppose, 65° C.

The same argument can be presented from a somewhat different viewpoint, taking the case of a homogeneous equilibrium. Consider an enclosed volume of two non-reactive gases. These may be considered to be in "equilibrium at any given temperature, yet obviously the type of equilibrium will vary with the corresponding change of temperature, the velocity of the molecules mean free path, kinetic energy and viscosity changing.

This demonstrates quite clearly the variation in properties with temperature necessary for the maintenance of equilibrium.—We are, &c.,

CLAUDE W. L. BOURLET
WIDGEY R. NEWMAN.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. clxxiii. No. 14.

"Action of the Infra-Red Rays on Phosphorescence." By M. Maurice Cuni.

No. 15.

"Absorption Spectrum of Oxygen." By MM. J. Duclaux and P. Jeantet.

"The Sub-bromide of Tellurium." By M. A. Damiens.

"The Constitution of the Polysulphonated Derivatives of Indigo." By M. Grand Monezin.

No. 17.

"A New Method of Determining Silica." By M. Travers.

"Dilromoanthraquinone used for the Synthesis of Alizarine." By M. Grand Monezin.

## NOTES.

ROYAL SOCIETY OF ARTS.—Meetings for the week ending November 26, 1921: Wednesday, Nov. 23, at 8 p.m.—"Trueman Wood" Lecture, "The Coming of Age of Long-Distance Wireless Telegraphy and some of its Scientific Problems,." by Prof. John Ambrose Fleming, M.A., D.Sc., F.R.S., Albert Medallist Alan A. Campbell Swinton, F.R.S., Chairman of the Council will preside. Friday, Nov. 25, at 4 p.m.—Dominions and Colonies and Indian Sections (Joint Meeting), "An Imperial Airship Service," by A. H. Ashbolt, Agent-General for Tasmania Brig.-General Lord Montagu of Beaulieu, K.C.I.E., C.S.I., will preside.

BLEACHING PALM OIL.—A very simple process has, it appears, given excellent results in Germany. It merely consists in moving a metal sieve, with fine meshes, upwards and downwards in the oil at a temperature of 100° C. Bleaching is produced by the frequently renewed atmospheric oxygen. Thus bleached, the oil could be utilised instead of coprah oil for alimentation.—*Revue de Chimie Industrielle,* October, 1921.

AN interesting paper by E. L. Nichols and D. T. Wilber has recently been published in the *Physical Review,* No. 6, xvii., June, 1921, on the "Luminescence of Certain Oxides Sublimed in the Electric Arc." From the synopsis it appears that "oxides prepared by sublimation are found to respond to excitation by cathode rays, as well as to flame excitation through a wide range of temperatures. The temperature at which excitation ceases is in general the same, taking each band separately, for flame excitation and for cathodo-excitation. The shift in the colour of luminescence is in general towards the violet with rising temperature. This shift is produced by the independent growth and decadence of over-lapping bands and not to any lateral movement of the bands themselves. Certain bands in the spectra of these oxides are most strongly excited by cathode rays at relatively high pressures, others appear as the vacuum becomes more complete, so that as exhaustion progresses there are marked changes in the colour of luminescence.

NEW BOOKS.—A new series of volumes, to be published by George Routledge & Sons, Ltd., under the title "Twentieth Century Chemistry," is in preparation under the Editorship of Sir William Tilden, D.Sc., F.R.S., Emiritus Professor in the Imperial College of Science and Technology, South Kensington, and Dr. J. C. Philip, F.R.S., Senior Secretary of the Chemical Society and Professor of Physical Chemistry in the Imperial College. The intention is to provide works of moderate size and price in all the more important sections of scientific chemistry, suitable for post-graduate readers and others possessing

sufficient elementary knowledge. The aim will be to produce readable and interesting books which, without being exhaustive monographs, will furnish advanced students with a complete survey of the present state of knowledge and opinion in each branch of the science. Several distinguished chemists, both British and foreign, have promised to assist by contributing volumes to the series.

New Method for Manufacture of Synthetic Nitrogen.—A new process has, according to *Chimie et Industrie*, been invented by an Italian, Dr. Caze, for manufacture of synthetic ammonia The requisite hydrogen is obtained by electrolysis of water and the nitrogen extracted from the air by a secret process by aid of an automatic machine working continuously. The two gases are combined at a low temperature in presence of catalysers. The works in Turin initially produced 300 kilogrms. of pure ammonia per diem. It was enlarged last December, and now produces 1000 daily. Finally the ammonia can be transformed into urea, which, as it contains 40 per cent nitrogen, is a very valuable fertiliser. In the invention of Prof. M. Andreucci of Rome, atmospheric nitrogen is obtained by the explosion of a mixture of 100 litres of air (containing 209 litres of oxygen) and 418 of hydrogen in an internal combustion engine (benzine; poor gas; lighting gas; or Diesel) provided with an electric system of ignition. The product obtained consists of approximately 336 grms. of water and 778·3 litres of almost pure nitrogen, with various foreign substances which are removed by chemical means. The motor utilised is adapted for the purpose by narrowing the air and hydrogen intake passages so as to obtain suction in the required proportion to prevent excessive pressures of explosion. A Watt indicator is utilised for the purpose — *L'Engrais*, July 22, 1921.

## New Patents.

This List is specially compiled for the *Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, W.C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

28557—Cumberland Coal, Power & Chemicals, Ltd.—Manufacture of ammonia sulphate, October 27.

28293—Jones, B. D.—Process for production of sodium pentaborate from boren ores. October 25.

28435—Kelly, A.—Treatment of mineral phosphates. October 26

28325—Society of Chemical Industry in Basle.—Manufacture of dye-stuffs of the triarylmethane series. October 25.

*Specifications published this Week.*

149001—Muth, G.—Process of preparing aluminium sulphate

127030—Westling, E. H.—Process for the production of manganese dioxide.

147909—Goldschmidt Akt. Ges.—Process for the production of ethylene chloride.

*Abstract Published this Week*

*Toluene Derivatives.* *Patent No. 169,025.*

A process for obtaining Toluene Derivatives is the subject of a Patent granted to Mr. A. D Clibbens, of Crumpsall Vale Chemical Works, Blackley, Manchester.

By the chlorination of toluene-p-sulphonic acid or monochlorotoluene-p-sulphonic acid in aqueous solution, a mixture of 2 5-dichloro and 2.5.6, trichloro-toluene-4 sulphonic acids is produced, from which the trichloro body is precipitated by neutralization with alkali, leaving the dichloro compound to be recovered by evaporation of the mother liquors. Instead of the free acids, their soluble salts may be used as starting material. On hydrolysis, the products yield 2.5-dichlorotoluene and 2 5.6-trichlorotoluene respectively.

*Sulphur Dioxide.* *Patent No. 168627*

A process for obtaining sulphur dioxide has been patented in this country by Mr. A. H Eustis of Milton, Norfolk, Massachusetts, U.S A. The product is obtained by separation from gas mixtures such as smelter smoke by absorption in and extraction from a liquid. The extraction from the liquid being effected by reducing the partial pressure of the sulphur dioxide in the atmosphere contracting with the liquid by diluting with a copious supply of gas such as steam which is condensible at lower pressure and/or higher temperature than sulphu dioxide.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

## NEW COMPANIES.

The under-mentioned particulars of New Companies recently registered are taken from the Daily Register compiled by Jordan & Sons, Limited, Company Registration Agents, Chancery Lane W.C.2.

Western Chemical Company, Limited.—(177674)—Registered 4th November, 1921 To carry on the business of Manufacturers and Dealers in Chemicals, Glues, &c. Nominal Capital £3,000 in 2,000 Ordinary Shares of £1 each and 4,000 Shares of 5s. each. Directors To be appointed by Subscribers. Qualification of Directors One Share Subscribers · J. S. Mason, Chester Cottage, Hassocks, Sussex; W. J. Knight, "Cantara", Field Way, Ruislip, Middlesex.

Hygeia, Limited —(177660)—Registered 4th November, 1921. 85, Gracechurch Street, E.C. To carry on the business of Chemists and Druggists. Nominal Capital £10,000 in 10,000 Shares of £1 each. Directors: To be appointed by Subscribers. Qualification of Directors. £300. Remuneration of Directors · To be voted by Company in General Meeting.

## NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemica Apparatus, &c., for review or notice to be addressed to the Editor.

**SUBSCRIPTIONS,** £1 12s. per annum, payable in advance should be addressed to the Manager.

**BACK NUMBERS and VOLUMES** can be purchased on application to he Manager.

THE CHEMICAL NEWS,
97, Shoe Lane, London, E.C 4.

## ADVERTISEMENTS.

**All communications for this Department should be addressed to—**

T. G. SCOTT & SON,
63, Ludgate Hill, London, E C.4.

THE CHEMICAL NEWS.
VOL. CXXIII., No. 3215

# THE COAGULATION OF COLLOIDS BY ELECTROLYTES.

By HUMPHREY D. MURRAY,
Exhibitioner of Christ Church, Oxford.

WHEN Graham first came to study colloidal substances, he noticed as one of their most characteristic properties their coagulation in the presence of electrolytes. Since that time more work has been done upon this particular aspect of the subject than possibly any other, and most workers seem to have realised that a true insight into the mechanism of coagulation will illuminate the whole subject of the stability of the colloid particle. The object of this paper will be to review the work done by various chemists upon coagulation, more particularly within the last few years.

Two series of experiments were carried out by Schulze (*Jour. Prakt. Chem.*, 1882, xxv., 431; 1883, xxvii., 320; 1884, xxxii., 390) and Linder and Picton (*Jour. Chem. Soc.*, lxi., lxvii., lxxi., and lxxxvii), which have had considerable influence upon all later work. Previous to this, Jevons (*Trans. Manch. Phil. Soc.*, 1870, p. 78) and Gouy (*Comptes Rendus*, 1889, cix., 102) had reached the conclusion that most colloid particles carried an electrical charge, and this belief has since been amply confirmed. These researches of Schulze and Linder and Picton made it plain that the factor which most directly influenced coagulation was the concentration of the ion bearing a charge opposite in sign to that of the colloid Moreover, it was found that trivalent ions were more effective in producing coagulation than divalent, and the latter in their turn were more effective than univalent ions. It was found, however, that there were distinct variations in the coagulative powers, or the reciprocals of the least concentration required to bring about coagulation, of ions of similar valency; but this variation seems rather to have been lost sight of in viewing the larger effect caused by difference in valency. Whetham (*Phil. Mag.*, 1889, xlviii., 474) suggested from the theory of probabilities that the coagulative powers of univalent, divalent and trivalent ions respectively would be in the ratio $x : x^2 : x^3$ where $x$ is some constant. This suggestion seemed to receive support at the time from the averaging of Linder and Picton's results, but as experimental work accumulated, its validity has been seriously called in question, until now it would seem safer scarcely to regard it even as a rough generalisation.

During their researches upon the negatively-charged arsenious sulphide Linder and Picton analysed the precipitate carried down when barium sulphate was added to the solution in in sufficient quantitiy. They found that the positive barium ion was entrained by the coagulum and intimately bound up with it, but that the sulphate ion was entirely absent. Experiments by other observers led to a similar conclusion, namely, that the coagulum always adsorbed a portion of that ion which was active in producing coagulation. Whitney and Ober (*Jour. Amer. Chem. Soc.*, 1901, xxiii., 842) confirmed the work of Linder and Picton, and came to the further conclusion that the active ions were always carried down in quantities which were equivalents. This would mean that each ion has a specific action of its own, and the decisive factor in conditioning coagulation is not necessarily its valency.

We can observe the action of salts in bringing about coagulation by examining the minimal quantity required, or by analysing the resulting coagulum, or directly by means of the microscope or ultra-microscope. This latter method has been employed by Cotton and Mouton ("Les Ultra-Microscopes"), Zsigmondy ("Zur Erkenntnis der Kolloide"), Galecki (*Zeit. anorg. Chem.*, 1912, lxxiv., 179), and others. Their researches have brought to light the fact that a small concentration of electrolyte causes no apparent increase in the size of the particles. Above this concentration the particles begin to condense, the larger serving as nuclei to the smaller, and the rate of condensation varies as the concentration of the colloid. This observation was borne out by Paine (*Proc. Camb. Phil. Soc.*, 1911, xvi., 430) working upon solutions of colloidal copper. He found that there was a definite initial period after the addition of the electrolyte when no coagulation occurred. When it started the rate varied as the square of the initial concentration of the colloid and also as some power of the concentration of the active ion. Some results by Galecki (*loc. cit.*) on solutions of gold sols are interesting. He added varying concentrations of $SrCl_2$ to a gold solution and examined th enumber of submicrons present in 1 cc. at the end of two days. On plotting the concentration of $SrCl_2$ against the number of submicrons, he failed to obtain smooth curves, but got curves of the general form shown in Fig 1.

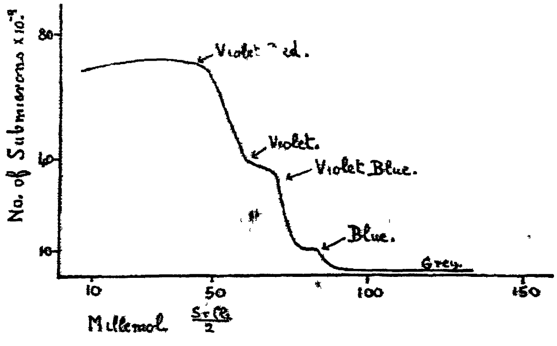



FIG. 1.

Similarly, on plotting the number of submicrons present in 1 cc. against the time elapsing after the addition of a definite quantity of $SrCl_2$, he obtained a curve of the form shown in Fig. 2. These curves were repeated with other electrolytes. They are interesting as seeming to show that coagulation, at least in the case of gold sols, takes place in stages, which are characterised by corresponding changes in colour.

The actual conditions under which the electrolyte has been added to the colloidal solution, and the subsequent treatment afforded to the resulting mixture, varied with each experimenter. In some cases the solution was titrated in the usual way

drop by drop; in other cases the mixture was made all at once, and the correct proportion found by trial and error. Sometimes the solution was shaken continuously during the addition; sometimes it was subsequently boiled. It

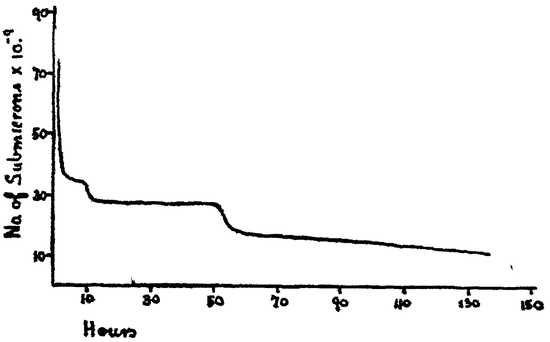



FIG. 2.

is not, therefore, permissible to compare the result of one worker with that of another. It should, however, be possible to compare one series so obtained with another; but when such a comparison is made we are met with numerous differences. To give but one instance—in the coagulation of arsenious sulphide, Linder and Picton (*loc. cit.*) deduce the following order for the coagulative power of the chlorides :—

$$Na < K. < NH_4 < H < Ni < Cd < Fe^{II} < Zn < Ca < Co < Sr < Ba < Mg < Hg < Pb < Fe^{III} < Al.$$

While Schulze (*loc. cit.*) deduces the order for the sulphates :—

$$K < Na < NH_4 < H < Mg < Fe^{II} < Ca < Mn < Ni < Zn < Al.$$

And Freundlich (*Zeit. Physik. Chem.,* lxxiii , lxxix,. lxxxiii., and lxxxvi.) :—

$$Li < Na < K < H < Mg < Ba = Zn = Be < Ca = Sr < Al = In = Ce.$$

This variation in results can be ascribed to several possible causes. In the first place we have seen that the larger particles act as condensation nuclei to the smaller, and therefore a large difference in the size of the biggest and the smallest particles present will lead to the appearance of flocks in the liquid with a concentration of electrolyte smaller than that required to begin coagulation with a colloid of uniformly fine grain. This fact has been emphasized by Odén (*Zeit. Physik Chem.,* 1912, lxxviii., 682). He found that the point of coagulation was sharper with a suspensoid of uniform grain, and also that a greater concentration of electrolyte was required to begin coagulation with a suspensoid of a fine grain than with one of a coarse grain.

An interesting series of experiments have been carried out by Weiser and Middleton (*Jour. Phys. Chem.,* 1919, xxiii., 630; 1920, xxiv., 30) and Weiser and Sherrick (*Jour. Phys. Chem.,* 1919, xxiii., 203) upon the coagulation of ferric hydroxide and aluminium hydroxide. They have come to the conclusion that adsorption of the electrolyte takes place, not only in the case of the charged particles, but also in that of the neutral substance. They found that, if the electrolyte were added slowly enough, a greater quantity was required to produce complete coagulation than if it were added all at once This extra quantity they ascribe to the amount of salt adsorbed by the flocks of colloid first coagulated. They also emphasize the fact that treatment of the solution in respect to shaking and change of temperature alters the amount of electrolyte required for coagulation. Weiser and Middleton also criticise Whitney and Ober's results showing that equivalent quantities of the active ion were carried down by the coagulum, and the grounds upon which Freundlich supported this view. Their results bear out the fact that adsorption is specific for each ion, but not that such adsorption is proportionate to the equivalents of the ions.

Until recently little attention had been paid to the absolute concentration of the colloid at the moment of precipitation, but Burton and Bishop (*Jour. Phys. Chem.,* 1920, xxiv., 703) have obtained a result previously indicated by Kruyt and Speck (*Koll. Zeit.,* 1919, xxv., 1) which in general would seem to show that this was of great importance. They studied the concentration of electrolyte necessary to produce coagulation in the case of solutions of $As_2S_3$, Cu, and mastic, when the concentration of the colloid varied. They found in the case of univalent ions that the concentration of the electrolyte varied inversely as that of the colloid, divalent ions were scarcely affected, while electrolytes, the active ion of which was trivalent varied directly as the concentration of the colloid. This result, they would suggest, is connected in some way with the concentration of the ion of same sign as that of the colloid. The effect of this ion has not generally been taken into account, but it must have some very definite bearing upon the subject. It may be noted in this connection that most colloidal solutions appear to have a saturation point and attempts to concentrate them beyond this point leads to continual coagulation of the colloid

It may be useful at this point to summarize the facts which appear to have an important bearing upon the whole theory of coagulation, and also the precautions which appear necessary to ensure comparable results in coagulation experiments. Of the first we have :—

1. The specific action of the ion of opposite sign to that of the colloid in adsorption, and in bringing about coagulation.
2. The greater effect in general of ions of higher valency.
3. The modifying action of ions of same sign as that of the colloid.
4. The possibility that equivalent quantities of different ions are entrained by the coagulum.
5. A minimal concentration of electrolyte necessary before coagulation begins.
6. The effect of an ion originally present in the colloidal solution, to which little attention has been paid

The precautions necessary to ensure uniform results which have already been discussed are :—

1. That the colloid have the same concentration in each case at the point of coagulation. This follows naturally if Burton and Bishop's work be found to have a general application.

2. That the electrolyte be quickly and uniformly mixed with the colloid. This may be facilitated by having the electrolyte in a dilute solution.
3. That the subsequent treatment of the solution in the matter of temperature and shaking be the same.
4. That the particles of the colloid be of uniform size.

It may be that these do not represent four independent conditions but that the variations introduced by their alteration are in some degree interdependent. Investigation of this fact should prove interesting and work on these lines is now being undertaken by the writer.

## BRITISH STANDARD SPECIFICATION FOR CREOSOTE FOR THE PRESERVATION OF TIMBER.

[THE British Engineering Standards Association have sent a copy of the recently-issued Specification for Creosote, which we are pleased to publish. The Report can be obtained from the Offices of the Association, 28, Victoria Street, S.W.1, price 1s. 2d. post free.]

This Specification covers the requirements of Creosote suitable for the treatment of railway sleepers and telegraph, telephone, and hangar poles.

TYPE A.

1. DESCRIPTION.—The material shall consist essentially of a distillate of coal tar, and shall be free from any admixture of petroleum or similar oils.

2. SPECIFIC GRAVITY.—(See Appendix I.). The specific gravity shall be not less than 1·015 and not more than 1·07 at 38° C. (100° F.) when compared with water at the same temperature.

3 FLUIDITY.—The material shall become completely liquid on being slowly warmed to 38° C. (100° F.) with stirring, and on cooling down shall remain completely liquid after standing for two hours at 32° C. (90° F.).

4. WATER CONTENT.—The amount of water in the Creosote shall not exceed 3 per cent when determined by the method described in Appendix II.

5. DISTILLATION.—When 100 cc. measured at 38° C. (100° F.) of the dry Creosote are distilled from a 250 cc. distillation flask (see Appendix III.) at such a rate that the distillation is complete in about 20 minutes, there shall distil at 760 mm. pressure,

| | | |
|---|---|---|
| up to 205° C. (401° F.) | not more than | 7 cc. |
| ,, 230° C. (446° F.) | ,, ,, | 40 cc. |
| ,, 315° C. (599° F.) | ,, ,, | 78 cc. |

the volumes of all fractions being measured at 38° C. (100° .).

The residue above 315° C. (599° F.) shall be soft and not sticky and its weight shall not be less than 22 grms

6. TAR ACIDS.—The amount of tar acids when determined by the method described in Appendix IV. shall be not less than 5 per cent and not more than 16 per cent by volume.

7. MATTER INSOLUBLE IN BENZOL (BENZENE).—The amount of matter insoluble in benzol (benzene) shall not exceed 0·4 per cent by weight.

ADDENDUM.—TYPE B.

*Alternative for Scotch Creosote.*

Scotch Creosote shall conform to the above Specification with the following exceptions:—

2. SPECIFIC GRAVITY.—The specific gravity shall be not less than 1 at 38° C. (100° F.). In the case of the blast furnace oil the specific gravity may be lower, but shall not be less than 0·940 at 38° C. (100° F.).

5. DISTILLATION.—The distillate at 315° C. (599° F.) shall be not more than 85 cc. and the residue not less than 15 grms.

6. TAR ACIDS.—There shall be no limit to the amount of tar acids.

APPENDIX I.

*Specific Gravity.*

Care shall be taken to ensure that the Creosote is completely liquefied and homogenous before the sample is taken.

In the event of the temperature at which the determination is made not being exactly 38° C. (100° F.) the observed specific gravity (d) at the temperature t° shall be converted to "corrected" specific gravity D by means of the formula:—

$$D = d + 0{\cdot}00075\ (t-38)$$

if t be in degrees Centigrade, or

$$D = d + 0{\cdot}00042\ (t-100)$$

if t be in degrees Fahrenheit.

APPENDIX II.

*Determination of Water Content.*

The material shall be made completely liquid and homogeneous by warming to 38° C. (100° F.). 100 cc. of the liquid measured at 38° C. (100° F.) shall be mixed with 50 cc. of Xylol previously saturated with water and the mixture distilled from a distillation flask at a rate of about 3 cc. per minute. 50 cc. of distillate shall be collected in a cylinder of suitable size graduated in 1/5 cc. and the volume of water determined at room temperature.

The condenser used in this test shall be either a straight vertical condenser, or of such construction that it will readily drain completely.

APPENDIX III.

*Distillation.*

The Creosote shall be dried over calcium chloride, plaster of Paris or other suitable material, and 100 cc. of the dried Creosote measured at 38° C. (100° F.) placed in a tared standard 250 cc. Wurtz distillation flask, the neck of which is approximately 12 cm. long with outlet tube emerging approximately half way up the neck. The flask shall be furnished with a standardised thermometer, the top of the bulb of which is just below the outlet tube. The distillation shall be carried out over a free flame. When a temperature of 315° C. (599° F.) has been reached, the distillation shall be stopped, the flask and contents allowed to cool, and then re-weighed.

*Correction for Emergent Thread of the Thermometer.*

The number of degrees C (dt) to be added to the observed thermometer reading t° C. shall be

calculated from the following formula :—

$dt = 0.000143 (t-t') N$, where N is the number of degree divisions of thread exposed above the cork and $t'$ the air temperature half way up the exposed thread.

When Fahrenheit thermometers are used, the formula shall be $dt = 0.0000794 (t-t') N$.

*Correction for Barometric Pressure.*

For every 25 mm. above or below 760 mm., 0·8 grm. (0·6 grm. in the case of Scotch oils) shall be subtracted from or added to the observed weight of residue in the flask.

APPENDIX IV.

*Determination of the Tar Acids.*

The tar acids shall be determined by complete extraction of the total distillate below 315° C. (599° F.) with caustic soda solution of specific gravity 1·18. The tar acids shall be separated from the soda solution by neutralising with sulphuric acid (specific gravity 1·35 at 15° C. (59° F.), *i.e.*, one volume of 1·84 acid mixed with two volumes of water) and their volume determined

## REPORT BY SIR PERCY GIROUARD, K.C.M.G. TO CLOSE BROTHERS & CO. LTD. ON THE OPERATIONS OF THE LOW TEMPERATURE CARBONISATION PLANT AT BARNSLEY, YORKSHIRE.*

*Low Temperature Carbonisation.*

FOR some years past I have been investigating the problem of the use of smokeless fuel, and though my studies have been mainly directed towards the use of coal in powdered form, a great development of which has been witnessed in the United States, my attention was also drawn to the various proposals for the low temperature carbonisation of small coals and slacks, which in all countries had a low value as compared with lump coal, and in some countries had practically no value whatever.

In June of this year I was asked by a mutual friend to look into the particular developments which had been carried out in England by Low Temperature Carbonisation, Ltd. Ascertaining that this organisation was the descendant of the original Coalite Companies, I was constrained to say that, though not antagonistic, as my knowledge of their operations was very limited, I could only enter into any investigation in a prejudiced spirit. Notwithstanding my attitude, you pressed upon me the national importance of the question, with the request that I should visit the Barnsley plant.

After my first visit, which proved of considerable interest, I informed you that if you desired me to go any further I should require complete independence in my investigations, and to be given the full confidence of the directors, staff, or engineers, and access to any documents I should require. This request was readily granted, and I may state at once that as from July until the present day one and all connected with the enterprise gave me every assistance and information I desired.

*Manufacture.*

On my first visit to Barnsley, where you had installed 20 retorts which were said to be capable of carbonising about 200 tons per week, I could not see the plant in actual operation, as it had been closed down in consequence of the coal strike. The strike perhaps had one advantage, it allowed of your introducing into the retorts a device which it was hoped would end one of the main difficulties which has always faced low temperature carbonisation, that of discharging the resultant Coalite (a smokeless fuel), which too often in the past had adhered so firmly to the walls of the retorts that extraction became a matter of the very greatest difficulty. In extreme cases it was freely admitted that several days passed after carbonisation before the coalite could be extracted. This led not only to high costs, but to the production of an inferior fuel, containing a high percentage of breeze.

The device, which I was enabled to see before its actual insertion in the retorts, consisted of a pair of collapsing plates which divided the coal charge into two halves. The plates were provided with holes at intervals throughout their surface. The coal was to be inserted in the retorts with the plates in an expanded condition, and means were provided by which they were readily collapsed. The results which were expected from this new and ingenious device were of the highest importance. It was expected :—

(1) That on collapsing the plates after carbonisation of the slack, the resultant Coalite would readily drop into a cooling chamber below;

(2) That during the period of carbonisation, the gases given off from the coal would readily escape through the orifices in the plates and not have to force themselves through a mass of hot coal occupying the whole retort;

(3) That the device would give a larger yield both of gas and of tar oils.

The hopes which were held out could not be ocularly demonstrated until a coal supply was available, and the retorts brought up to a low temperature heat, which was to be about 550° C. within the retorts.

The strike having ended, coal was shortly available, and the heating of the retorts was started early in August, and in the week ending August 25, 13 tons of coal were carbonised. From that week to the present day, the progress has been continuous, and in the last three weeks, ending October 6, approximately 150 tons of slack per week were carbonised, resulting in approximately 100 tons of Coalite per week, and a yield of 15-18 gallons of tar oils per ton of coal carbonised. During the whole period, from the starting of the retorts to date, 833 tons have been carbonised. Manufacture on such a scale cannot be considered to be of an experimental or laboratory character.

The devices which have been introduced have, therefore, had a very severe test, and they have gone through it with great success, more particularly under the circumstances of starting a new plant. Many difficulties militated against abnormal success. The washing appliances were not, and are not now, by any means perfect, and the

* Sir Percy Girouard's Report on the Low Temperature Carbonisation of Coal Slack is a matter of national interest, and with his permission and that of Messrs. Close Bros. & Co., at whose works the experiments were carried out, we are reproducing it in full.

fuel is therefore, at times, admitted to the retorts with too high a degree of moisture.

Other mechanical defects revealed themselves from time to time, but all are quite capable of explanation and perfection. The plates acted exactly as was expected. The collapsing, which is effected by a mechanical device actuated from outside the retorts, has acted with precision, and allows of the discharge of the carbonised material with almost unfailing regularity.

The main factor which has in the past obstructed the progress of low temperature carbonisation would appaer to have been entirely solved. The yield of tar oils has even exceeded anticipation.

During the period a mechanical defect arose which allowed of a very important investigation One of a pair of the cast-iron plates broke away from its fastening and had to be replaced This allowed of an examination of the plate, which had been under heat for some three weeks. Its condition was perfect, and there is little doubt that such plates will endure low temperature heats for a long period without oxidisation. The mechanical defect which allowed of this accident was easily remedied.

So much for the retort and its discharge, both of Coalite and by-products.

A second ingenious addition had also been introduced. In many of the former plants the Coalite on discharge was treated much in the same way as metallurgical coke and quenched in the open. This not only gave the material a bad appearance, but led to the formation of a great deal of breeze. In the present design this has been entirely obviated. The Coalite is discharged into an enclosed cooler surrounded by water, and after a due period the cooler itself is emptied, when the Coalite is found to be in a hard, compact form, containing not more than 5 per cent of breeze. So durable is the material produced, that it suffers very little in transport, and several hundreds of tons have been transported long distarnces, notably to London, without suffering any ill effect.

At an early period in the carbonisation it was found that it would be an advantage, not only mechanically, but financially, to mix the more expensive caking slacks, which form a binder for the whole material, with a proportion of noncaking slack, which often is a material of very much lower value. The proportion has been followed, until to-day 70 per cent. of non-caking slack is being used. I have little doubt that practically all the Yorkshire and Derbyshire coal slacks could be used by themselves, but on the financial side it is highly desirable to mix In a few instances it is necessary to do so.

*By-Products.*

The by-products of low temperature carbonisation have been well known for many years, but mainly on a laboratory scale, as there has not been any large quantity available for commercial tests It is perfectly clear that they contain, primarily, a rich gas of high B.T.U. value. The motor spirits are said to amount to about 3 gallons, of a specific gravity which would apparently place them somewhere between petrol and benzol.

The tar oil, as a whole, burns readily. It can be fractionated into Diesel oil, lubricating oil, and cresylics, all having a high potential value. On distillation, apparently 50 per cent of the tar oil yields will be pitch, which in itself is more than likely to contain material of high commercial value. Ten tons of tar oils are now being fractionated at a high temperature tar distillery, and the results will shortly be available, but as it took many years of careful research to determine the values of high temperature tar, it is too much to expect that low temperature tar oils have as yet been fully analysed.

A leading Institute of Technology, dealing with the commercial aspect of the value of tar and tar oils, has expressed a desire to carry out a series of commercial and technical experiments, now that large quantities are likely to be available.

*Engineers' Report.*

Your engineers have been engaged upon furnishing a report which is now available, and as I have followed its preparation closely from week to week it is not difficult for me to give you my general comments upon it. From what I have already said, you will gather that my own independent observations support, in so far as they have gone, everything of the same character mentioned in your engineers' report.

One of the most interesting portions of the report, as it affects your immediate and future developments, is their estimate of cost, which they give in their Exhibits No 3 and No. 5 (these Exhibits are given in a balance sheet).

On the Expenditure side, in Exhibit No. 3, one figure of the highest importance is the price at which this side of the balance sheet should be debited for slack. This figure I have always though of as the "X" of the whole calculation, but it here taken at the high figure of 12s. 6d., which by no means represents the figure which a colliery company establishing a low temperature carbonisation plant would debit to expenditure. There are countries even to-day where these slacks are practically given away, and yet such slacks can be converted into the most highly-priced coal —domestic fuel—sold in London at 60s., and even more. It is quite equal to anthracite, which is sold at even a higher figure.

The cost of carbonisation would appear to be reasonable and quite comparable with such costs in high temperature plants. Such a comparison, however, is misleading. Owing to the low temperature utilised and to other factors, the cost should be lower in your plants.

On the Revenue side, Coalite is taken at 50s. per ton at the works. This is an "X" figure again, depending upon the market value of coal, and it would appear reasonable in the present state of trade for domestic fuels, more particularly when it is realised that Coalite has a radiant value for domestic purposes quite 30 per cent better than the best coal, and this is borne out by Government experiments.

The tar oils have been given a value of 6d. : a conesrvative figure, but one which it is desirable to adopt in such a balance sheet.

Only 1 gallon of benzol is credited, that which comes off with the gas.

Exhibit No. 5 has been prepared to show the effects of a reduction in the price of coal, etc., to figures approaching more normal conditions.

I have followed very closely the preparation of these costs, which have been made out for a plant

carbonising 100 tons of coal per day as against the present small battery of 20 retorts with its 30 tons a day (necessarily using a considerable amount of manual labour), and they would appear to be fair and reasonable

*Conclusion.*

I am persuaded that the working of the battery of twenty retorts established at Barugh, continuously and progressively up-to-date, is not only a great step in advance in low temperature carbonisation, but has provided all the data necessary on a commercial scale to warrant your placing the information you now have available before any interested countries or enterprises. It has provided the certainty of the manufacture from slacks of a smokeless transportable fuel of even a higher value than the best domestic coal, and this product alone, in a balance sheet where slack is debited at its proper value, would yield a handsome return, the gases and oils remaining as a factor of safety.

But there are other and very important aspects of low temperature carbonisation which have come out very prominently during the success of this battery. I refer here to its use as an industrial fuel.

The lines of investigation adopted for this purpose have been clearly indicated by your engineers and very promising developments may be witnessed at an early date.

The whole industry, if developed on the lines which you have initiated, would appear to be one of paramount national importance. It may, with the least interference in the proper standard of wages, lead towards the greatest necessity of the country—a cheap standard fuel, domestic or industrial—incidentally smokeless, thus, not only assisting the gradual revival of industry, but also improving the condition of our atmosphere and the health of our people.

Coal is the one great asset which allows of an excess of population beyond the natural feeding capacity of our country on these small islands. If used rationally, it is of much more importance to the British people than the discovery of any other mineral.

Is it too much to hope that when it is fully realised that such a development will only be ancillary to the other great fuel and power industries of the country, that these interests will be the first to come forward and recognise that we may be on the verge of a new era in the use of our most vital asset?

## THE AIMS AND BOUNDARIES OF PHYSIOLOGY.*

By SIR WALTER M. FLETCHER, K.B.E, M.D Sc.D, F.R.S

(Concluded from p 271)

MEANWHILE, the chemical structure, no less than the material form, of the body was being explored, and here, too, progress followed the path of nalysis, ever more refined and complete. Just as old notions of "humours" of the body had been resolved into varieties of cell activity, so the vague chemical ideas conveyed in the words "protoplasm" or "metabolism" received precision by expression in terms of colloidal systems or of associated enzymes or catalysts in appropriate positions, effecting chemical changes of recognisable type among substances of relative simplicity.

Along these lines of analysis rapid progress has been made, but it is to be observed that it has been in great part along diverging lines. The tendency has been centrifugal, or, to use a biological simile, the growth of physiology has led to fissiparous habit. Pursuit of knowledge by particular technical methods has led to specialism; men have reached points far distant along branches of inquiry that at first grew together from the stem. The very development of new technical methods may by itself lead unavoidably to separatism, for the microscope and test-tube may best be used in rooms widely different in equipment and often far separated in space. So have grown up new-named sciences within a science, and the histologist or cytologist, the neurologist, the pharmacologist, the biochemist—each carrying off, so to speak, his part of the subject—may be found to be incurring the dangers or even paying the penalties of schism.

Step by step, however, with this progress in analysis, a continual advance towards synthesis has accompanied it as new truths have been unfolded to the investigator. Here, as in other fields, the conception that the whole is the same as the sum of its parts is either meaningless, or, if it have any meaning, is untrue. Fresh reinforcements have steadily come to the idea that the animal body is not to be rightly considered as a patchwork of the activities of its parts, but that the organism itself as a whole is the true physiological unit. In this conception the functions of the organs and of their own cellular subdivisions can only find due expression in relation to each other and to the functions of the whole. Just in proportion as analysis has proceeded with ever greater refinement to trace in terms of physics or chemistry the nature of given organic or cellular phenomena, the analysis itself is found to be pointing to new relationships between part and part of which the meaning is bound up in the unity of the organism.

Of this continued absorption of analytic data into synthetic conception, this interweaving of increasingly manifest diversities into an increasingly emergent unity, illustration can be found in many directions. The name "hormone" has been given to chemical products of particular organs which pass by way of the blood to stimulate another organ or other organs of the body to changes in activity. This mode of chemical regulation by messenger, so to speak, is superadded to the more rapid method of regulation by nervous impulse through the nervous system: and already many beautiful examples of delicate interplay and co-ordination have been discovered between the two kinds of regulation. In its earlier phases the knowledge of these messengers gave us a picture of relatively simple, though wonderfully adjusted acts of chemical regulation. As analysis of the hormonic exchanges of other glands and tissues of the body has proceeded, however, a system of interplay and reciprocal function of increasing complexity has been revealed by later studies. Our knowledge of this is still young and quite rudimentary, but at every fresh step in this advance it becomes more evident that the multiplying facts can only be resumed by a conception

* Address delivered before Section I, British Association (Edinburgh Meeting).

of the whole organism as a unit of which the parts exist to preserve the integrity and "normality."

In the study of the nervous system, again, new methods of observation and analysis have given us during the past half-century immense additions to our knowledge of the intricate fabrics of the brain and spinal cord and of the functions of the various systems of fibres and cells. The content of our knowledge of these must be tenfold that which was known fifty years ago. Here again, as investigation has gone forward, and as analysis has proceeded by methods so special and so refined that neurologists work, as it were, in a field of their own, it has proceeded only to reveal ever more and more clearly what Sherrington, one of the chief pioneers in this analysis, has himself called the "integrative" action of the nervous system. The fabric of nerve cell and fibre, whether we trace its history from the lower to the higher animals, or whether we trace its complexity in the individual, is revealed to us as a series of superimposed controlling systems whose structural relations find intelligible expression only in terms of functions, and of functions of the animal as a whole

Is the same return to synthetic conceptions to be found as a result of analysis of the biochemist? His work has brought much simplification to our notions of the chemistry of the body. We have learned that in the exchanges within the living cell we are not necessarily, or indeed probably, dealing with molecules of a complexity unknown outside the living body; we do not now think as formerly of substances being worked up through successive stages of elaboration into a living molecule—a molecule of "protoplasm" of mystical complexity—or of other substances reappearing as the result of incessant degradation of parts of the living molecule. Analysis has shown already that many characteristic cell-changes turn upon relatively simple reactions of a kind familiar in chemistry between known and relatively simple substances. How much further will this analysis proceed? No doubt many of the typical functions of particular kinds of cell will become expressible in a set of chemical formulæ, and every simplification attained by the biochemist in terms of known chemical or physical law will be a notable gain. Yet even now we can feel assured that the analyses of the biochemist bring with them new emphasis upon the essential unity of the whole organism. Let me give but one illustration of this. In the studies of immunity from disease it had long been known that substances which to a chemist would appear to be identical could be sharply distinguished in the most decisive way by biological reactions. Tiny fragments of a small blood-clot can be made thus to declare whether they come from a man or from what other animal, when no chemist would have dreamed of finding a distinction. Dudley and Woodman have lately been able, however, to bring biochemistry within the range of this biological delicacy of discrimination, and have shown a subtle difference in the chemical architectures of the caseins derived respectively from the milk of a cow and of a sheep. More recently the two modes of analysis have been brought side by side. Similar cells in similar organs of the two not widely dissimilar birds, the hen and the duck, secrete layers of egg-albumin during the completion of that wonderful structure, the egg. From the "white" of each egg can be prepared apparently identical albumins, and in a pure crystalline form. This albumin is built up in each case from simple materials—amino-acids—derived from the food, and we should naturally expect a close similarity between the two kinds of resulting albumin, that in the hen's egg and that in the duck's The most refined methods of ordinary chemical examination show us, indeed, that the two are chemically identical and indistinguishable, containing on analysis the same amounts of the same varieties of amino-acids. But Dakin has lately succeeded in tracing a difference between the two albumins, exhibited only as partial differences in the order or pattern in which some of the constituent amino-acids are linked together in the structure of the albumin molecule. By using a physiological test, Dale, at the same time, has been able to show a decisive and even dramatic difference between the qualities of the two albumins so near to chemical identity. By using the "anaphylactic" reaction of the organic tissue from an animal "sensitised" against hen albumin, he has found that a suitable application of hen egg-albumin will produce a decisive response, while an exactly similar dose of duck egg-albumin will produce no effect whatever; and so *vice versa.* Here, then, is some authentic stamp of unknown kind imposed uniformly upon the parts of the organism of a given species, even upon the molecules of the albuminous coating of its egg. We are brought sharply back from the relative simplicities of chemical analysis to consider this supra-chemical impress of specific pattern, a phenomenon which can have no meaning that is not drawn from a conception of the organism as a whole.

It would be impossible here, and quite unnecessary for the present purpose, to do more than refer finally to the beautiful researches of recent years upon the modes of regulation of breathing, upon the gas exchanges of the blood, and upon the associated activities of other organs, and especially of the kidney, which have brought such ample support and illustration to the doctrine first clearly taught by Claude Bernard, namely, that the different mechanisms of the body, various as they are, have their single object in "preserving constant the conditions of life in the internal environment." These regulative functions in particular have been fully discussed by Dr. Haldane in a recent notable essay, and he has shown how, as their chemical analysis has proceeded and observations have been collected by physiological methods, themselves of a delicacy often far exceeding those of present physical and chemical methods, it has become more and more necessary to express the facts in terms of an organic unity. "The physical and chemical picture is entirely obliterated by the picture of organism." These considerations are full of interest, of course, in their relation to the rival mechanistic and vitalistic theories that have been advanced for the explanation of living processes. Here, however, I refer to this synthetic tendency of modern physiology because of its practical bearing upon the present development of the subject in the universities and the medical schools. As the preliminary analyses of the functions have been, as we

have seen, centrifugal and fissiparous in their tendencies, so the accompanying and inevitable synthesis, resuming analytical data within the notion of organism, has been centripetal and conjugative. It is this bond of organic unity which must sooner or later serve to bring together the scattered workers in different fields of analysis. It is this conception of the organism, moreover, which must maintain physiology as a great primary branch of study—the study of the living organism.

If physiology remains as a free subject of university study, we need not have serious fear that the fissiparous, centrifugal tendencies already noticed will be dangerous or crippling. Ludwig organised his physiology teaching at Leipzig in 1846 under the three main divisions of histology, experimental work, and physiological chemistry. In the English revival that we have earlier sketched, this grouping, largely under the influence of Foster, was maintained not only at Cambridge, but at other centres here and in America. As years have passed, however, there has been an increasing tendency here to follow what is commonly done in other countries, and to place histology with anatomy. In my personal view, physiology cannot proceed without perpetual use of the microscope, and yet anatomy must be dead without histology. I should hope to see histology the well-worn bridge of union between the two subjects, just as, I think, we should look to cytology and the study of cell development to offer active points of growing union between physiology and the sciences of animal and plant morphology. These and other questions of detailed organisation will, I hope, be explored fully in the discussion for which we are hoping to-day. With time also has come a great development of biochemistry, and this, if only from the structural necessities of its laboratory technique, is tending more and more to set up house for itself. This, too, is to be a matter for fuller discussion presently We may perhaps hope to see in biochemistry as it grows not only a common meeting-ground and an unfailing source of new inspiration for physiologists and pathologists alike, but also a pathway by which organic chemistry may be led towards the study of living matter. Few organic chemists in this country, though more in America, have been led by that path till now, and yet we must believe that biochemistry has perhaps even more to give to organic chemistry, as we now know it, than it has to gain. A study of organic compounds in a spirit of detachment from the living processes which gave them birth must surely lead often to mere virtuosity in the laboratory transformations of chemical structure, and I venture very timidly to think that many signs point to the near approach of a time when organic chemistry will feel the need of fresh inspiration coming from the intricate laboratory of the living cell In a university the separation of laboratories, which must be guided solely by convenience, as convenience is dictated by necessary differences in equipment and technique, may be easily transcended by the free communication of workers in different branches. Intellectual association and close co-operation, and especially within a university, seem inevitable, as we have seen, because of the converging approach of diverse workers in common reference to the conception of organic unity. There can be no boundaries to physiology narrower than the limits of the study of the whole organism and the balanced regulation of its living parts.

I would venture here, however, to point to some dangers by which the sound development of physiology seems to be threatened, that spring from its necessarily close association with medical education, dangers eminent in the present stage of rapid growth in medical studies both here and, even more obviously, in America. Historically, physiology may be said to have been born of medicine, but it has sanctions and a strength quite independent of the great services it has rendered and has still to render to the material good of mankind through medicine, and, in a less, though in no insignificant degree, to agriculture. We may recall that chemistry, too, was almost equally born of medicine; medicine, at least, was the foster-mother and long the nurse of chemistry. Lyon Playfair, in his inaugural address of 1858, in this very place, said, nevertheless, that "chemistry in her period of youth, full of bloom and promise, was forced into a premature and ill-assorted union with medicine." We can now look back and see that chemistry, in becoming free of medicine, and in becoming a great independent branch of learning, has, by the fruits of that freedom, repaid to medicine a thousandfold her early debts of the nursery. So, too, the history of the last half-century, in which physiology has become an independent subject of university study, shows how this freedom has multiplied the gifts which physiology has had it in her power to return to her ancient mother. There can be no dissolving of the ties between one and the other, but we must see to it that these ties are well-adjusted and that there shall be no "ill-assorted union" between the two.

In the rapid growth of medical schools throughout the English-speaking world there are present signs that the essential part which physiology plays in medical education and study may wrongly masquerade as the only service physiology has to give to man, and may appear to fill the measure of her rightful status. In more than one of the great American universities physiology is treated either in theory or in practice as a subject within the Medical Faculty to be housed within the Medical School, yet at the same time not as a subject in the Faculty of Arts or of Science, nor to be studied alone or with other sciences as part of a liberal and non-professional education. It is rare in the United States for physiology to be studied by any but professed medical students, and there is some reason to think that it is becoming rarer in Great Britain than it was a few years ago.

To my mind this tendency is to be deplored It implies a reversal of that growth of physiology in freedom which began half-a-century ago and from which such good fruit has already been gathered. It has two chief evils among its inevitable results. Removed from its position among other university subjects by geographical separation that in some universities amounts to transporation and exile, it is deprived of the kinship and co-operation of the sciences touching its own boundaries—those of zoology, embryology,

and botany, of agriculture, of psychology, of physics and chemistry. Assigned, if not limited, to a place in the medical curriculum, it is apt to be narrowed in its claims and outlook, and to lose not only its proper neighbours, but even parts of itself, whittled away in the organisation of a purely medical programme in the guise of pharmacology, neurology, toxicology, and the like, for which special funds may be available, separate places in the time-table reserved, and independent departments provided. But a second evil strikes more deeply. Any arrangements that give in effect a restriction of physiological studies to medical students alone must be doubly injurious. It is injurious to the general course of education, because it tends to cut away from the other university students the opportunity of possessing themselves, either as a primary or secondary study, of the knowledge and discipline of physiology which has educative value in the highest degree for the cultural or the practical sides of living. And here, secondarily, we may notice the loss to an applied study only less in importance to that of medicine; I mean the science and practice of agriculture. It is injurious, again, to physiology itself, because we know well from reiterated experience how many promising recruits for the future advancement of the subject have been brought to it, often, as it were, by chance, in the course of their university life, attracted to it whether from classical studies or mathematical, or from other branches of natural science. A notable number of the chief leaders in the science of the past and present generation have so been attracted, without any previous thought of medical studies as such, whether these have been added later or not; of these, not a few whose names are well known to us all have never become, in the technical sense, students of medicine at all. They may have lost by this, but should we willingly have lost them?

I hope that what I have earlier said with regard to the great service that physiology has both to give to medicine and to receive from it will acquit me of any charge of desiring less, rather than much more, intimacy and intercourse between them. I believe that no better service can be done for the good of both than to increase their mutual offices and the ties between them. But we must see that, in uniting physiology to medicine, we do not uproot it from that soil in which alone it can abundantly flourish and bear fruit, the environment of a university with all that connotes If there be any serious doubt of the reality of the dangers I have indicated, I would point to the dearth of men fitted to promote and teach the subject among those coming from the schools in which physiology is regarded as a medical study and no more, and is not given its full university status. In the United States at present there is a grave and admitted dearth of suitable candidates for chairs of physiology, in spite of the remarkable work which has been done there in recent years and the fine material equipment in general available. I venture to offer my conviction that the prime cause of this shortage is the absence of the great recruiting possibilities of university life and the undue limitation of physiology to medical students. Men coming to physiology as a "preliminary subject" and nothing more are not likely to think of it as their life-work, but will pass through it not to return.

Let me, in conclusion, point again to the highest of the tasks which physiology, like every other science, has to perform. Its highest and indeed its primary task is to enlarge the vision of man and to enrich his knowledge of truth. The secondary tasks of physiology in finding power through truth, power to diminish pain and to restore health, and to guide to right and prosperous living are happily so beneficient in kind, and already in some degree so fruitfully discharged, that it is not easy, or indeed common, to keep in mind that great and primary aim. Right thinking in this respect is the only constant guide to right action in all the practical questions which confront us now in our discussion of the position and the future of this science. "Man does not live by bread alone": and we shall find—we have already abundantly found in experience—that it is only through the seeking of wisdom first that power to increase the comfort and convenience of life is most fully to be won. The practical services of inquiry have been easy for all to see. Men have come readily to think of physiology as the handmaid of medicine and as nothing more. Of late years we who follow the study of living things have not had interpreters to make plain to men at large the interest and beauty of the additions to revealed truth which have been coming from the work of the investigator. There are very few among the onlookers who have seen, or who can bring others to see, those clearer visions of the consummate beauty which are being revealed in the study of the body, visions as remote from the actual figments daily painted for us by our sense organs as are the newest visions of the physical world, yet appealing as strongly to the intellectual and æsthetic emotions. Few hold the quest for natural knowledge in right relation to other activities of the mind; few see it not merely and not in chief as a useful pursuit of power, but in its essence as a pursuit of truth

That knowledge of natural truth and of the changing pattern of our ideas of the natural world should be an unusual or quite subordinate part of a cultural equipment, in this and in recent generations, may be due to lack of interpreters, but it is due also to convention and educational habit, and these, perhaps, combine in special degree to shut out from the world of general culture the revelations of intricate beauty in the living body of man. Ancient and mistaken theological conceptions filtering through the Victorian age have tended to degrade the dignity and marvel of the body. Generations that have been nurtured upon narrowed classical studies have so far forgotten the spirit of Greece as to ignore the universal beauty of truth; it has been thought vulgar not to know the verbal details of an old mythology, but hardly respectable not to be ignorant of the elementary laws of life and of the unseen beauties of the body unfolded in modern study. So have many submitted to be enchained in ignorance and superstition as to vital matters of reality, victims of every passing charlatan. Out of this loss of instruction in the beauties and wonders of living substance, as they are becoming known, must come great loss of possible happiness, and indeed there come, too, a loss of

dignity, for we may fitly apply the rebuke of Robert Boyle, much more deserved now than in his darker century, who held it to be "highly dishonourable for a Reasonable Soul to live in so Divinely built a Mansion as the Body she resides in, altogether unacquainted with the exquisite Structure of it."

Meanwhile the workers will proceed in their quest for further truth, caring little if, for the time being, other eyes are blind to its beauty. They will still be lured by it as all eager minds have been lured before; some will confess the attraction of a call for help in human need and suffering, some will claim austerely that they follow only the bidding of a curiosity of mind, and some perhaps may work for fame. But, whether they know it or not, the effective lure that Nature holds out to those of her followers who have it within them to respond to it, and so to reach new knowledge, is a quickening hint of further beauty to be unfolded in further truth. Whether they know it or not, they might make the same Confession as that of St. Augustine: "And I replied unto all those things which encompass the door of my flesh, 'Ye have told me of my God, that ye are not He: tell me something of Him.' And they cried, all with a great voice, 'He made us.' My questioning them was my mind's desire, and their Beauty was their answer."

## IMPERIAL WAR RELIEF FUND.

### Letter to Graduate Members of the Universities of Great Britain and Ireland.

Many men distinguished in letters and science are suffering great privation in Austria to-day, and the present condition of student life is a matter of grave concern for the future welfare of Europe. It is the problem presented by this serious situation that called into activity the Universities' Committee, at the instigation of Lord Robert Cecil. This Committee has appealed to the Universities of Great Britain and Ireland to come to the assistance of the Professors and Undergraduates in the war-stricken areas of Europe. The British Universities are responding generously; the sum of £1 per head per student is being gradually raised, giving to date a total of £32,000; this has been done mainly by student effort. The money is being spent in a carefully organised plan for the relief of the most destitute students in the Universities of Austria, Hungary, Poland, Czecho-Slovakia, &c., and in giving a certain amount of food and clothing to the Professors and Lecturers of the Austrian Universities.

The plea for help for Senior Members of the Universities of Austria has not met with such a wide response as the plea to students for students. This we feel sure is partly due to a feeling that such small gifts as Graduate Members can afford to give may be of insignificant value We are, however, in a position to point out that any sum subscribed is valuable. The average Viennese Professor, with wife and children, draws but the equivalent of £40 to £60 per year to maintain himself and his family. From the Armistice to the end of last year one-tenth of the Professors and Lecturers of Austria died, largely as a result of want, starvation, and consequent disease. We feel that no further comment is necessary.

The Universities' Committee, whose appeal to students on behalf of students has received such an encouraging response, is asking an equal effort on the part of men of learning in Great Britain and Ireland in the work of relieving the distressed Senior Members of sister Universities. Men who are famous throughout the civilised world, Exner, Tchermak, von Lang, Palisa, Strygowski, Wilhelm, Klein, Fuchs, Fried, Ebner, Charlemont, Lorenz-Liburnau, and many others, are finding very great difficulty in carrying on their work. If every man and woman who has had the privilege of studying in this country would give £1 1s., the staffs of the Austrian Universities would be at least sure of adequate nourishment for themselves and their families.

(*Signed*) William Bragg, Bryce, A. S. Eddington, Richard A. Gregory, Haldane of Cloan, Frederic G. Kenyon, Walter Lock, Donald Macalister, Charles J. Martin, Henry A Miers, Gilbert Murray, E. Rutherford, M. E. Sadler, Arthur Schuster, Napier Shaw, A. E. Shipley, George Adam Smith, Ernest H. Starling, J. J. Thomson.

Since the above signatures to this appeal were given, facts as to the conditions obtaining among the men of science and learning in Russia have been brought to our attention. Between 1914 and 1920, 30,000 doctors died through war and pestilence. The need for doctors, scientific men, engineers, agriculturists, &c., is vital to the country. Through seven years of war and revolution, with almost complete severance from Western Europe, Russia has been reduced to a position dangerous to civilisation. Famine of an intensity unparalleled in human record has devastated the country. The American Relief Administration and other funds are bending all their energies on trying to save the children. The Universities' Committee, in co-operation with the British Committee for Aiding Men of Letters and Science in Russia, hope also, with your assistance, to relieve some of the most acute distress obtaining in the Universities of Russia.

Cheques should be made payable to the Hon Treasurer, Universities' Committee, and sent to the Organising Secretary, at Fishmongers' Hall, London Bridge, E.C.4.

Eleonora Iredale, *Organizing Secretary.*

## NOTES.

Royal Institution.—The Ninety-Sixth Christmas Course of Juvenile Lectures, founded at the Royal Institution in 1826 by Michael Faraday, will be delivered this year by Prof. J. A. Fleming, F.R.S., on "Electric Waves and Wireless Telephony." The Lectures, which will be experimentally illustrated, will be given on the following days at 3 o'clock: Thursday, December 29, "Surface Waves on Liquids"; December 31, "Waves in Air"; January 3, "The Telephone"; January 5, "Electric Oscillations"; January 7, "Electric Waves,"; and January 10, "Wireless Telephony."

THE OPTICAL SOCIETY.—In addition to its ordinary programme, the Optical Society has arranged a series of special meetings to be devoted to subjects dealing with the evolution and development of various types of optical instruments. The Science Museum, Kensington, possesses a most interesting, and in many respects, unique collection of such instruments, with the characteristics of which instrument makers and users might well be more familiar. By arrange-with the Museum authorities, these instruments will be available at the meetings for purposes of illustration and demonstration. The first meeting of the series will be held at the Imperial College of Science and Technology, on Thursday, Nov. 24, 1921, at 7.30 p.m., when Prof. F. J. Cheshire, C.B.E., will deal with "Polarising Apparatus." Other subjects to be discussed at future meetings include "Microscopes" (Prof. A. Pollard), "Telescopes" (Mr. D. Baxendall), "Astronomical and Surveying Instruments" (Mr. L. C. Martin).

## MEETINGS FOR THE WEEK

*Monday, November 28.*

Royal Society of Arts, 8. (Cantor Lecture). "Processes of Engraving and Etching," by Arthur M. Hind.
Faraday Society, 8. "The Effect of Cold Work on Commercial Cadmium," by J. Neill Greenwood. "Reaction between Cathodic Hydrogen and Nitrogen at High Pressures," by J. N. Pring and E. O. Ransome. "The Electrolysis of Aqueous Solutions of Alkaline Nitrites with a Lead Anode and an Electrometric Determination of the Constitution of the Complex Anion Formed," by F. H. Jeffery. "An Inhibition Period in the Separation of an Emulsion," by T. C. Nugent. "Induced Reactions and Negative Catalysis," by N. R. Dhar and N. N Mittra Dr. S. Judd Lewis and Miss F. M. Wood will exhibit and describe "A New Adjustable Thermostat for all Temperatures between 0 and 100 deg. Cent."

*Wednesday, November 30.*

Royal Society of Arts, 8. "The Preservation of Stone," by Sir Frank Baines

*Thursday, December 1.*

Institution of Electrical Engineers, 6. "The Cyc Arc Process of Automatic Electric Welding," by L. J. Steele and H. Martin.

## NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemical Apparatus, &c., for review or notice to be addressed to the EDITOR.

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THE CHEMICAL NEWS.
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## THE PRESENT POSITION OF THE THEORY OF DESCENT, IN RELATION TO THE EARLY HISTORY OF PLANTS.*

By H. D. SCOTT, LL.D., F.R.S.

IT has long been evident that all those ideas of evolution in which the older generation of naturalists grew up have been disturbed, or, indeed, transformed, since the re-discovery of Mendel's work and the consequent development of the new science of Genetics. Not only is the "omnipotence of Natural Selection" gravely impugned, but variation itself, the foundation on which the Darwinian theory seemed to rest so securely, is now in question.

The small variations, on which the Natural Selectionist relied so much, have proved, for the most part, to be merely fluctuations, oscillating about a mean, and therefore incapable of giving rise to permanent new types. The well-established varieties of the Darwinian, such as the countless forms of *Erophila verna*, are now interpreted as elementary species, no less stable than Linnean species, and of equally unknown origin The mutations of De Vries, though still accepted at their face value by some biologists, are suspected by others of being nothing more than Mendelian segregates, the product of previous crossings; opinion on this subject is in a state of flux. In fact, it is clear that we know astonishingly little about variation.

My friend, Dr. Lotsy, indeed, proposes to dispense with variation altogether, and to find the true origin of species in Mendelian segregation; inheritable variability, he believes, does not exist; new species, on his bold hypothesis, arise by crossing, and so, as he points out, we may have an evolution, though species remain constant Thus everything apparently new depends on a re-combination of factors already present in the parents. "The cause of evolution lies in the interaction of two gametes of different constitution."

I am aware that very surprising results have been obtained by crossing. Nothing could well have been more striking than the series of *Antirrhinum* segregates which Dr. Lotsy showed us some years ago at a meeting of the Linnean Society. And now we hear of an apetalous *Lychnis* produced by the crossing of normally petaloid races. We do not know yet to what extent that sort of thing goes on in Nature, or what chance such segregates have of surviving. Still, if one may judge by Dr. Lotsy's experimental results, ample material for Natural Selection to work on might be provided in this way (see Dr. Lotsy's book, "Evolution by Means of Hybridisation, The Hague, 1916).

Dr. Lotsy's theory that new species originate by Mendelian segregation, if true, would have the advantage that it would make quite plain the meaning of sexual reproduction. Hitherto there has been a good deal of doubt; some authorities have held that sexual reproduction stimulated, others that it checked variation. But, if we eliminate variation, and rely solely on the products of crossing, we get a clear view—"species, as well as individuals, have two parents"; sexual reproduction can alone provide adequate material for new forms, and can provide it in unbounded variety.

Again, though Dr. Lotsy himself is far from sanguine on this point, the crossing theory might be helpful to the evolutionary morphologist, for breeding is open to unlimited experiment, and we might hope to learn what kinds of change in organisms are to be expected. For example, the *Lychnis* experiment shows how easily a petaloid race may become apetalous. Such results might ultimately be a great help in unravelling the course of evolution in the past. We should gain an idea of the transformations which might actually have taken place, excluding those which were out of the question. At present all speculation on the nature of past changes is in the air, for variation itself is only an hypothesis, and we have to decide, quite arbitrarily, what kind of variations we think may probably have occurred in the course of descent. One need only recall the various theories of the origin of the seed from the megasporangium to realise how arbitrary such speculations are.

But, while recognising certain advantages in the theory of the origin of species by crossing, it is not for me to pronounce any opinion as to its truth It is only the present position of the question that concerns us to-day. We shall hope to hear a statement of Dr. Lotsy's views from his own lips.

Some modern geneticists believe that there is evidence for mutation by the loss of factors, apart from the effects of crossing. Dr. Lotsy considers that such changes, if proved, can afford no explanation of progressive evolution. "Evolution by a process of repeated losses is inconceivable." It has, however, been pointed out by Dr. Agnes Arber, in her recent admirable book on water-plants, that, on any theory of evolution, "what organisms have ganied in specialisation they have lost in plasticity." She avails herself of a human analogy and says: "The man, though superior to the baby in actual achievement, is inferior to it in the qualities which may be summed up in the word 'promise'," just as the Angiosperm, though its degree of differentiation so greatly exceeds that of the primordial protoplasmic speck, is inferior to it when judged by its power to produce descendants of widely varying types (p. 335).

This is true, but it is not clear that this admitted loss of potentialities is the same thing as the loss of factors, in the sense of genetics. For example, if a glabrous variety of Violet really arose as a mutation by loss of the factor for hairiness, assuming that such a loss was permanent, the effect would seem to be a diminution of specialisation, though, no doubt, it might also be interpreted as a loss of potentiality.

Turning for a moment to Darwin's own theory of the origin of species by means of natural selection, the efficacy of the latter, in weeding out the unfit, is, of course, still acknowledged, and some geneticists allow is a considerable rôle. But there is a strong tendency in these days to

* Address delivered before Section K, British Association (Edinburgh Meeting).

admit natural selection, only as a "merely negative force," and as such it has even been dismissed as a "truism." Now Darwin's great book was most certainly not written to enunciate a truism. He regarded natural selection as "the most important, but not the exclusive, means of modification" ("Origin of Species," p. 4). It was the continual selection of the more fit, the "preservation of favoured races," on which he relied, and not the mere obvious elimination of the unfit, and this great idea (so imperfectly understood by many of his contemporaries and successors) he worked out with astonishing power, in the light of the changes which man has produced, with the help of his own artificial selection.

It may be that the theory of natural selection, as Darwin and Wallace understood it, may some day come into its own again; certainly it illuminated, as no other theory has yet done, the great subject of adaptation, which to some of us is, and remains, the chief interest of biology. But in our present total ignorance of variation and doubt as to other means of change, we can form no clear idea of the material on which selection has had to work, and we must let the question rest.

For the moment, at all events, the Darwinian period is past; we can no longer enjoy the comfortable assurance, which once satisfied so many of us, that the main problem had been solved—all is again in the melting-pot. By now, in fact, a new generation has grown up that knows not Darwin.

Yet evolution remains—we cannot get away from it, even if we only hold it as an act of faith, for there is no alternative, and, after all, the evidence of palæontology is unshaken I have thought it fair to lay stress on the present state of uncertainty in all that concerns the origin of species. On another occasion I even ventured to speak of the return of "pre-Darwinian chaos." But out of this chaos doubtless light will come.

Last year we had a joint discussion on Genetics and Palæontology; among many good speeches, I specially remember a remark by Miss Saunders, our then President, that Mendelism is a theory of heredity, not of evolution—a caution not unneeded, though as the crossing hypothesis shows, the connection between the two conceptions may prove to be a very close one

Genetics is rendering the greatest service to biology generally in ensuring that organisms shall be thought of as races, not as isolated individuals, mere chemical and physical complexes, at the mercy of the environment. The whole tendency of modern work is to show that in living things heredity is supreme. An organism is what it is by virtue of the constitution of the germ-plasm derived from its parents. As Dr. Church has said in one of his recent Botanical Memoirs: "The individual is no longer to be regarded as an isolated unit, or a casual creation, but is the present representative of a 'race'." That is to say, the individual is not, as short-sighted chemical physiologists tend to believe, a mere physical mechanism, the creature of the external environment to which it passively responds! but it is the living presentation of a continuous line of organism, successful since living, or a "race" leading back as the expression of continued response to very similar, but not necessarily identical, environment, in unbroken plasmatic continuity, over a period of time which, in terms of ultimate cytological history, may represent a continuous reaction and record for anything up to such an inconceivable period as two thousand million years." This expresses the case vigorously, whether we accept the time estimate or not. Dr. Church goes on to say that "during this period the more fundamental reactions, as expresed in morphological units of construction, have been established as constants beyond any hope of change" (Form Factors in Coniferæ, Oxford, 1920, p. 22). This last statement is an important one for the palæontologist, for all our attempts to trace descent rest on the assumption that, in a general sense and as regards certain well-established characters, "Like breeds like"

History, then, broadly speaking, is everything. But there is more than one kind of history in biology. First, we have the exact records of the Mendelian from generation to generation, $F^1$, $F^2$, and so on; this alone is adequate, but we usually have to be content with something much less. At the other end of the scale there is the fossil history full of gaps and uncertainties of every kind, but always imposing from its vast duration. Then there are intermediate kinds of biological history, such as the imperfect records of the breeding of cultivated plants or domestic animals. These can sometimes now be interpreted in the light of the more exact genetic histories, as Dr. Lotsy will show us in the case of some neglected and misinterpreted observations of Darwin. "Domestication," as he says, "spells segregation, followed by selection and isolation of the desirable segregates." Darwin himself, though necessarily groping in the dark where genetics were involved, yet thought the study of cultivated and domestic races the best clue to the origin of species. If this holds good still, it makes a strong point in favour of the crossing theory of evolution, for the history of cultivated races seems to be largely the history of deliberate or unconscious Mendelian crossings. We may reasonably expect to find a relation between the process of origination of new cultural races and that of new species in Nature.

This suggests the question, what we mean by a "species"—far too difficult a matter to discuss now. Whatever we may think of Darwin's theory, his "Origin of Species" is at any rate a classic, and I believe we cannot do better than continue to use the word in the same sense as Darwin used it—*i e.*, essentially in the sense of a Linnean species.

Perhaps the best answer to the question "What is a species?" is in the form "*Ranunculus repens*," avoiding all attempts at definition. I know Dr. Lotsy thinks differently, but pure races, whatever else and however important they may be, "are but rarely or never met with in Nature" (Lotsy), and are certainly not *species* in the classical sense in which Darwin used the word; to my mind it seems a pity to go out of our way to change completely the meaning of a familiar term. We can continue to call "pure races" by that name or any more modern equivalent, and "elementary species" may still be called so, or I have no objection to calling them "Jordanons."

In the interests of practical taxonomy they necessarily have to be kept subordinated to Linnean species. There are difficulties enough either way, but they are, as it seems, less if we adopt the conservative course. That many Linnean species are real units of a definite order is generally admitted. Dr. Lotsy himself dwells on their distinctness, which depends on their usually not inter-crossing, and appears to be shown by the fact that among animals members of the same species recognise each other as such and habitually breed together. Such habitual breeding together under natural conditions is perhaps the best test of a species in the Linnean sense. "The units within each Linnean (=species) form an inter-crossing community" (Lotsy). He adds: "Consequently it is Nature itself which groups the individuals to Linneons" These "pairing communities" have recently been re-christened by Dr. Lotsy "syngameons", a good name to express this aspect of the old species (Lotsy, *La Quintessence de la Théorie du Croisement.* Archives Néerlandaises des Sciences, Sér. III. B., 1917, iii.).

I do not propose in these brief remarks to venture on that well-worn subject the inheritance of acquired characters—*i.e.,* of such characters as are gained during the lifetime of the individual by reaction to the environment. There has always been a strong cross-current of opinion in favour of this belief, especially in our own time, in the form of "unconscious memory", so ably advocated by Samuel Butler and supported by Sir Francis Darwin in his Presidential Address to the British Association at Dublin. Prof. Henslow, as we all know, is a veteran champion of the origin of plant structures by self-adaptation to the environment. On the other hand, some geneticists roundly deny that any inheritance of somatically acquired characters can take place. In any case, the evidence, as it seems, is still too doubtful and inadequate to warrant any conclusion, so, however fascinating such speculations may be, I pass on.

To bring these introductory remarks to a close, we see that while the theory of descent or evolution is undisputed, we really know nothing certain as to the way in which new forms have arisen from old. During the reign of Darwinism we commonly assumed that this had happened by the continual selection of small variations, and we are no longer in a position to make any such assumption.

We have been told on high authority that "as long as we do not know how *Primula obconica* produced its abundant new forms it is no time to discuss the origin of the Mollusca or of Dicotyledons" (Bateson). Yet this is just the kind of speculation in which a palæontologist is apt to indulge, and if kept off it he would feel that his occupation was gone! However, so long as we may believe, as already said, that, on the whole, like breeds like, that grapes do not spring from thorns, or figs from thistles, there is perhaps still sufficient basis for some attempt to interpret the past history of plants in terms of descent. But certainly we have learnt greater caution, and we must be careful not to go far beyond our facts, and, in particular, to avoid elaborate derivations of one type of structure from another where the supposed transitional forms have but a purely subjective existence; we have realised the difficulty of tracing homologies. We may still be allowed to seek affinities, even where we cannot trace descent. And though we may sometimes fo a little beyond our tether and give rein to bolder speculations, there is no harm done so long as we know what we are doing, and there may be even some good in such flights if our scientific use of the imagination serves to give life to the dry bones of bare description. On this subject I am somewhat more optimistic than Dr. Lotsy, who, abandoning his "Stammesgeschichte" point of view, has dismissed all attempts at phyligenetic reconstruction as "fantastic."

There are some questions of the highest interest that at present can scarcely be approached in any other but a speculative way. Within the last year or two, new points of view have thus been opened out. For example, Dr. Church's able essay on "Thalassiophyta and the sub-aerial transmigration" has brought vividly before us the great change from marine to terrestial life.

The origin of a land flora had, of course, been discussed with much ability before, but rather as incidental to a morphological theory. Dr. Church puts the actual conquest of the land in the foreground. We watch the land slowly rising toward the surface of the primeval ocean, the rooted sea-weeds, succeeding the free-swimming plankton, and then the continents slowly emerging and the drama of the transmigration as the plants of the rock-pools and shallows fit themselves step by step for sub-aerial life when the dry land appears. It is a striking picture that is thus displayed to our view—whether in all respects a faithful one is another question; we must not expect impossibilities. The doubts which have been raised relate first to the assumed world-wide ocean, which seems not to be generally accepted by geologists. If continental ridges existed from the first (*i.e.,* from the original condensation of watery vapour to form seas), the colonisation of the land may have followed other lines and have happened repeatedly. Perhaps, after all, that would not greatly affect the botanical aspects of the transmigration.

The other difficulty is, however, a botanical one. Dr. Church looks at the whole problem from the sea-weed point of view, and it is well he does, for sea-weeds have been badly neglected, especially by some of the great continental morphologists, who used to lead our speculative flights. Dr. Church is much impressed by the high organisation of many sea-weeds, especially in the living marine flora, by that of the Brown Algæ. Here we find well-differentiated leaves special reproductive shoots, extremely efficien holdfast roots, and sometimes a definite alternation of generations, while, on the anatomica side, we meet with true parenchymatous tissues a well-developed phloëm and secondary growt in thickness There is, in fact, in many respects an anticipation of, or an analogy with importan features which characterise the higher plants o the land.

Dr. Church believes that the chief morphological characters of the land flora were firs outlined in the sea; that such characters wer not newly assumed after transmigration, but tha

they merely represent an adaptation to sub-aerial conditions of a differentiation already attained at the phase of marine phytobenthon (rooted sea-weeds). At the same time it is not suggested that any existing class of sea-weeds can be taken as representing the ancestry of the land flora; the transmigrant races are, as Algæ, extinct—they may have been Green Algæ of a high grade of organisation, on a level now perhaps most nearly represented by the highest of the Brown Seaweeds.

Thus the transmigrants, which were destined to become the parents of the land flora, are pictured as already highly organised and well-differentiated plants, which only needed to provide themselves with absorptive instead of merely anchoring roots, and with a water-conducting system (xylem and stomata) in order to fit themselves for sub-aerial life, while, on the reproductive side, the great change remaining to be accomplished was the adaptation of the spores to transport by air instead of by water.

It is clearly impossible to criticise the theory in detail, for the assumed transmigrants are *ex hypothesi* unknown; we can only form a distant conception of what they were from the analogy of the highest sea-weeds of the present day, which admittedly belong to quite different lines of descent. Dr. Church puts the transmigration so far back (pre-Cambrian) that not much help can be expected from fossils, but to this subject we shall return

Some botanists find a difficulty in accepting the suggestion that plants already elaborately fitted out for a marine life could have survived the transition, however gradual, to a totally different environment. Such thinkers prefer to believe that lower forms may have been more adaptable, and that morphological differentiation had, in a great degree, to start afresh when the land was first invaded. My own sympathies, I may say, are here with Dr. Church, for I have long inclined to the belief that the vascular plants were, in all probability, derived from the higher Thallophytes. The view of the late Prof Lignier, now so widely accepted, that the leaf, at least in the megaphyllous or fern-like vascular plants, was derived from specialised branch-systems of a thallus, assumes, at any rate, that the immediate ancestors possessed a well-developed thallus, such as is now known only among the higher Algæ The Hepaticæ, as we now know them, clearly do not come into the question, and the Pro-hepatics, which Lignier postulated as early ancestors, have only a theoretical existence, and if they were ever present in the flesh may well have been transmigrant Algæ.

The question now arises, how far have we any evidence from the rocks, which may bear on the transmigration and on the nature of the early land flora? A very few years ago no such evidence was available—such data as we then possessed seemed too obscure to discuss. Quite recent discoveries, especially those from the famous Rhynie Chert-bed, have shown that in early Devonian times certain remarkably simple land-plants existed, which in general configuration were no more advanced than some very ordinary sea-weeds of the present day. At the same time, these plants were obviously fitted for terrestial life, as shown by the presence of a water-conducting tissue and stomata, and by the manifestly air-borne spores. These simplest land-plants are the Rhyniceæ (*Rhynia* and *Hornea*), while the third genus, *Asteroxylon*, was more advanced and further removed from any possible transmigrant type.

My friend Dr. Arber was so impressed by the primitive character of *Rhynia* (the only one of these genera then known) that he boldly called it a Thallophyte, while recognising, in respect of anatomical structure, an intermediate position on the way to Pteridophyta. This is not really very different from the view taken by the investigators themselves, though they call the plants Pteridophytes, which they certainly are, if we go by internal structure rather than external morphology. But if, as Kidston and Lang suggest, the Rhyniaceæ "find their place near the beginning of a current of change from an Alga-like type of plant to the type of the simpler vascular Cryptogams, they must have been very primitive indeed and might even be regarded as fairly representing the true transmigrants which had not long taken to the land. (This view is further developed and expanded in the authors' fourth memoir, which I have had the privilege of reading in MS.).

It is true that the middle Devonian is much too late a period for the original transmigration (I believe there is some evidence for land-animals in the Lower Silurian), but one may argue that some of the transmigrant forms may have survived as late as the Devonian, just as the *Selaginella* type seems to have gone on with little change from the carboniferous to the present time. There must have been many such survivals of earlier forms in the Devonian period, if Arber was right in regarding all the characteristic plants of the *Psilophyton* Flora as "much more probably Thallophyta than Pteridophyta ("Devonian Floras: A Study of the Origin of Cormaphyta," Cambridge, 1921, p. 47). Certainly some of them, apart from the Rhyniaceæ, have an alga-like appearance (*e.g.*, *Pseudosporochnus*) and there is some evidence that such plants also were vascular. There is, in fact, no doubt that the earlier Devonian Flora is turning out to have been on the whole more peculiar and more unlike the higher plants than we realised a few years ago. The early Devonian plants cannot usually be referred to any of the recognised groups of Pteridophytes, and this is not owing to our imperfect knowledge, for it is just in those cases where the plants are most thoroughly known that their unique systematic position is most manifest. Arber called all the plants in question "Procormophyta"—an appropriate name. As Kidston and Lang point out in their later work, the three groups—Pteridophyta, Bryophyta, and Algæ—are brought nearer together by the Rhynie fossils.

And yet there is evidence that about the same period stems with the highly organised structure of Gymnospermous trees already existed. I refer to remains of which *Palæopitys Milleri*, from the Middle Old Red Sandstone of Cromarty, is the type. We need much further investigation of these higher forms of early Devonian vegetation, but we know enough to impose caution on our speculations.

The Rhyniaceæ, at all events, were leafless and rootless plants. In one species of *Rhynia* and in

*Hornea* the aerial stems are entirely without any appendages, while in the other *Rhynia* there are hemispherical swellings, which have been identified by Arber with certain states of the spines in *Psilophyton.* The emergences of *R. Gwynee-Vaughani* have been interpreted as nascent leaves, but more recent observations, showing their late histological origin, have rendered this hypothesis very doubtful.

In *Asteroxylon*, a higher plant altogether, the stem is clothed with quite distinct leaves, though they are somewhat rudimentary as regards their vascular supply. Have we, in these plants, and others of contemporary date, the first origin of the leaf from a mere non-vascular emergence, or had reduction already been begun, so that in Rhyniaceæ, for example, the leaves were in the act of disappearance? In the former case we should be assisting at the birth of Lignier's phylloids, the microphylls of the Lycopod series, though, as just mentioned, the outgrowths in *Rhynia Gwynne-Vaughani* may have had nothing to do with leaves.

But the opposite view may also be tenable. We have already seen that these plants have been referred both to the Pteridophytes and the Thallophytes; they also show signs of Bryophytic affinities, and I understand that it has even been proposed to include them in the Bryophyta, in which case every possible view will be represented. The *Sphagnum*-like structure of the columellate sporangium or sporogonium of *Hornea* and *Sporogonites* may justify the Bryophytic attribution, and it is then, of course, easy to extend it to *Rhynia.* If we were to adopt this opinion, we should probably have to regard these simple Devonian plants as representing stages in the reduction of the sporophyte to a sporogonium, the leaves being already nearly or quite lost, while the branched thallus was still much in excess of the simple seta of the modern Moss or Hepatic. Naturally we know nothing of the gametphyte, so that the material for comparison is limited Kidston and Lang, however, have recently pointed out that the presence of spore-tetrads clearly indicates the existence of a gametophyte.

I make no attempt to decide between these views. There can be no reasonable doubt that the Psiliphytales generally represent an earlier phase of Cormophytic life than any of the groups previously recognised. But we must not assume that *all* their characters were primitive. It has been pointed out that the Rhyniaceæ were peat plants, and that the peat-flora is apt to be peculiar. Under such conditions it is not improbable that a certain amount of reduction may have already been undergone, though this is not the view taken by the investigators.

(To be continued.)

## THE MICROCHRONOGRAPH.*

By Prof. R. A. SAMPSON, F.R.S.

THE instrument described is in actual use at the Royal Observatory, Edinburgh, for registering clock times of any signal accurately to 0·001 sec., for the purpose of examining short-period changes in the relative rates of two clocks, or the lag of a controlled clock, or of one part of a piece of apparatus with respect to another. It has many other applications. The means employed are an adaptation of the oscillograph; this instrument can be so constructed as to be completely free from noxious or variable lag of its own. A detector is placed between the poles of a powerful electro-magnet This detector consists of a short loop of fine platinoid wire, under tension, and spanned by small plane mirror. The clock signal or other signal being given as an electric current of a few milliampères is recorded photographically on a moving film by help of a minute rotation of the mirror. The rate of motion of the film cannot be trusted for fine measurement over an interval of one second; therefore the standard is taken from an interrupter which cuts off the light falling on the mirror at intervals of approximately 0·1 sec. This interrupter is a simple steel tongue, set in vibration and not maintained in any way, and carrying a wire which occults a slit through which the light passes.

The scale employed can be varied within wide limits. That used most frequently at present gives a motion of the film of about 3·3 cm. per second, with a lateral displacement of 0·13 mm per milliamp., corresponding to a magnification of the movement of the wire loop of the detector by about 1000.

Exhaustive tests have shown that the instrument is completely reliable.

* Read before the British Association (Edinburgh Meeting), Section A.

## ULMITE, A CONSTITUENT OF BLACK SANDSTONE.*

By THOMAS STEEL.

AT various points along the coast of New South Wales there occur frequent outcrops of a black friable sandstone. The positions of some of these in the Richmond River district are indicated on maps published by the New South Wales Department of Mines (Ann. Rept., 1895, p. 151; 1896, p. 155).

At Tweed Heads a thick bed is exposed on the north bank of the river near the township, from which the sample described in this paper was obtained. There is no igneous rock near the deposit, which is covered by a layer of ordinary sand of varying thickness. Water collected in wells dug in the overlying sand is brown in colour.

The rock is very friable, rubbing readily between the fingers to a sharp sand. On ignition a fragment crumbles to loose sand and becomes white. A portion heated in a glass tube yields water having a strongly acid reaction.

Under the microscope the rock is seen to be built up of worn sandgrains of fairly uniform size, each of which is covered with a thin dark-coloured film resembling a coat of varnish. Gentle friction suffices to remove the coating from the sand grains. On lixiviating the pulverised rock the dark coating can be readily separated and obtained quite free from sand and, when dry, forms a dark brown powder. Microscopically this shows as irregular flakes of vary-

* From the *Proceedings of the Linnean Society*, New South Wales Vol. xlvi, Part II, May 25, 1921.

ing thickness, the inner ones being structureless and of a translucent brown colour, while the thick ones are black and opaque. The translucent flakes do not affect polarised light, and as will be shown, chemical examination proves the substance to consist of humus or humic acid. The powder is readily and completely soluble in caustic potash, soda, or ammonia, forming a clear deep-brown liquid, which, on acidifying with sulphuric or hydrochloric acid, deposits a copious brown flocculent precipitate, leaving the solution moderately coloured. In strong sulphuric acid the dark powder dissolves readily, particularly on slightly warming, forming a clear, very dark-brown solution, which, on being poured into a large volume of water, throws down a copious soft brown precipitate, leaving the solution only slightly coloured. In strong nitric acid, the powder dissolves readily, but no precipitate is produced on dilution with water nor on neutralisation with alkalies. Even on boiling, the substance is only sparingly soluble in strong hydrochloric acid.

When the precipitate obtained by dilution of the solution in strong sulphuric acid is drained on a filter, the resulting slimy mass is readily soluble in water and also in strong spirit, giving a solution resembling caramel. The water solution obtained in this way, when treated with barium hydrate or carbonate becomes colourless, the substance being carried down along with the barium sulphate. The dark-brown solution obtained by treating a dilute solution of soda or potash with excess of the substance, is readily precipitated with alcohol, the supernatant liquid having still, however, a fairly dark colour. A solution in potash, on neutralisation with sulphuric acid, avoiding excess, remains clear and is precipitated by addition of alcohol. The precipitate may be thoroughly washed with dilute alcohol (Sp. Gr. 0·86), after which it dissolves readily in water, the solution so formed not being precipitated by alcohol, but, if a small amount of potash or soda be added, alcohol produces a copious precipitate, leaving the solution only slightly coloured. The aqueous solution of the alcohol-washed precipitate gives brown precipitates with most metallic salts, precipitation being complete, also with the hydrates and salts of barium, calcium, and strontium, with the alums, and with bromine water. Iodine, tannin, and starch solutions produce no precipitate.

Amongst the few metallic salts which do not cause a precipitate are mercuric chloride and ammoniacal nitrate of silver. The colour is removed by shaking with hydrates of iron and alumina and with litharge, manganese dioxide, animal charcoal, and ordinary soil, previous ignition of the soil making no difference. When shaken with sand the solution is decolourised, the colour, however, being absorbed entirely by the fine clayey portion of the sand, the coarser grains being inert. The same applies to treatment with the black sandstone, after ignition, but if sand or soil is boiled with hydrochloric acid and washed so as to remove soluble mineral matters, the residue is quite inert.

The substance can be salted out of solution with a number of salts, sodium chloride, and sulphate, ammonium sulphate, nitrate and chloride and others, leaving the solution but faintly coloured. From concentrated solutions, acetic acid causes practically complete precipitation in a well curdled form, but from dilute solutions the precipitate is slimy but equally complete.

The barium compound prepared by precipitating the water soluble preparation with baryta water, washing with alcohol, and drying, corrected for associated mineral matter, contains 41·3 per cent. barium oxide.

The pulverised air-dry rock yielded the following figures to proximate analysis:—.

| | |
|---|---|
| Water ... ... ... ... ... ... | 1·63 |
| Loss on ignition .. .. ... ... | 8·19 |
| Sand ... .. .. .. ... ... | 89·50 |
| Soluble in hydrochloric acid .. | 0·68 |
| | 100·00 |

When the coating from the black sandstone is lixiviated until quite free from sand and air-dried, it has the following proximate composition:—

| | |
|---|---|
| Water at 150° C. .. . . . . . | 17·3 |
| Loss on ignition . . | 67·6 |
| Mineral .. . .. . . . . | 15·1 |
| | 100·00 |

On boiling 0·5 grm. with 50 cc. N/10 caustic soda and titrating back with corresponding sulphuric acid, 24·7 cc of neutralisation was obtained.

This preparation, after drying at 150° C., calculated free from mineral matter, gave the results below, on ultimate analysis. Humus is known to have a somewhat variable composition according to source and method of preparation. When made from sugar, for instance, ti may be quite free from nitrogen. For comparison I have inserted analyses of humus from a number of sources, references to which are given.

*Analyses of Humus Derived from Various Sources.*

| | (1) | (2) | (3) | (4) |
|---|---|---|---|---|
| Carbon ... | 50·53 | 57·75 | 53·42 | 52·71 |
| Hydrogen ... | 5·67 | 5·43 | 5·16 | 3·98 |
| Oxygen ... | 43·20 | 36·02 | 40·92 | 41·49 |
| Nitrogen ... | 0·60 | 0·80 | 0·50 | 1·82 |
| | 100·00 | 100·00 | 100·00 | 100·00 |

(1) Black sandstone. New South Wales.
(2) Brown peat. Watt's "Dict. Chem.", 1879, viii, p. 649.
(3) Decayed fir wood. *Jour. Chem. Soc.*, 1906, Abs. ii., p. 388.
(4) Decayed oak wood. *Jour Chem. Soc.*, 1906, Abs. ii., p. 388.

A preparation of humus made by treating black soil from Blackheath, N.S. Wales, with potash, and precipitation with sulphuric acid, behaved in all respects in a manner identical with the black sandstone preparation.

I would propose the name Ulmite for this form of humus as found coating sandstone grains.

Samples of black sandstone were supplied to me by Mr. W. S. Dun, of the Department of Mines, from McAuley's lead, Esk River; Iluka, Clarence River; and Sans Souci, near Sydney. They were in all respects similar to my specimen from Tweed Heads.

A similar coating to the above occurs on the rounded grains and pebbles of rock phosphate which constitute the surface "soil," four to six inches in depth, on Ocean Island (*Jour. Soc. Chem Ind.*, 1921, xl., p. 59T).

## THE REACTION OF IRON WITH NITRIC ACID.

By JOSEPH G. BROWN.

IN previous papers the theory was advanced that the rate of solution of iron in nitric acid of different density is associated with different chemical reactions. This theory was based upon the study of a voltaic cell having an iron anode and with nitric acid as an electrolyte. In general it was concluded, (1) that the rapid rate which takes place in dilute acid is associated with the formation of ferrous nitrate; (2) that the moderate rate which occurs in acid of intermediate density is associated with a ferrous reaction involving some other product than ferrous nitrate; and (3) that the very slow rate in concentrated acid is associated with a ferric reaction.

The chemical products of this reaction and of the electrolysis of nitric acid were investigated by Freer and Higley in 1899. Veley and Manley measured the electrolytic conductivity of nitric acid in 1898. Young and Hogg measured the reaction rates of the process in 1915.

A consideration of the results of these studies and of the properties of the iron and nitrogen oxides and hydroxides has led to a more detailed theory of the action of iron with nitric acid.

Iron forms three known oxides: ferrous, ferric, and ferroso-ferric; and three hydroxides: ferrous, ferric, and meta-ferric. The hydroxides are amphoteric, *i.e.*, they act either as weak bases or weak acids. This indicates that they ionise either with hydroxyl or hydrogen ions and probably with both. The ease with which iron compounds change valence and the tendency which they have to form compounds with mixed valence are well known.

Nitrogen forms five oxides: pentoxide, peroxide, trioxide, nitric and nitrous, and in combination with hydrogen, amine oxide and ammonium oxide. These oxides unite with water to form the series: nitric acid, nitrous acid, hyponitrous acid, hydroxyl amine, and ammonium hydroxide. Dilute nitric acid is one of the strongest acids known, while ammonium hydroxide and hydroxyl amine are bases. The intermediate compounds are weak acids.

A study of the properties of water solutions of nitric acid, of their action in electrolysis, and their reaction with metals, indicates that as the density increases the acid characteristics become weaker, and the basic characteristics become stronger, thus showing the amphoteric nature of nitric acid.

The reduction products which result when iron is dissolved in dilute acid are shown to be the consequence of the action of hydrogen ions in decreasing the valence of nitrogen. In consequence of this reduction electrons are removed from the iron by No+ and N+ ions. In concentrated acid, however, the hydrogen ion concentration is small, hence the reducing action upon the nitrogen does not occur. This results in electrons being removed from the iron by the $No_2$+ ions, which, on account of their oxidising character, increase the valence of the iron, thus forming ferric ions before any reaction takes place.

The observations are best accounted for by assuming that in concentrated acid the reaction is basic, *i.e.*, that the iron ions unite first with with hydroxyl ions.

The products of the electrolysis of nitric acid solutions and the formation of the passive condition when an iron anode is used in the electrolysis, are in strict agreement with these conclusions.

It is believed that the principles involved in this theory are of general application. Chromium forms a series of oxides similar to iron but with an additional acid forming oxide. When chromic acid is used as an electrolyte in the cell with an iron anode, the results are similar to those obtained with concentrated nitric acid. No matter how dilute the chromic acid solution may be, there is no indication that the acid reaction takes place. This might be expected since chromium compounds show a more strongly amphoteric character and chromic acid is much weaker and more oxydising than nitric acid.—*Physical Review*, October, 1921.

## STELLITE.*

By ELWOOD HAYNES.

REALIZING many years ago that an alloy that would take a cutting edge and at the same time resist the action of the atmosphere would fill a long-felt want, I made attempts even then to produce such a mixture or combination of metals. I found, however, that the problem was beset with many difficulties. Alloys containing copper were always subject to the tarnishing action of moist air and sulphuretted hydrogen; mixtures containing nickel and copper only possess the same disadvantages, though to a limited degree. Aluminium alloys with copper and nickel gave considerable hardness and a very high elastic limit, but they would tarnish in moist air, particularly in the presence of hydrogen sulphide.

In 1891 I made an alloy of nickel and tungsten, and, while this was not immune to acids, it resisted atmospheric influences remarkably well. This alloy was made by melting pure tungsten and pure nickel in a small crucible composed of a mixture of pure alumina and pure magnesia. The fusion was made in a small furnace of my own construction. The fuel used was natural gas, using air blast from a small foot-bellows.

Later, in 1898, I produced pure alloys of nickel and chromium by the reduction of their mixed oxides with pure aluminium. The alloy of nickel and chromium thus formed took a high polish, and retained its lustre in boiling nitric acid when the chromium constituted more than twelve to fifteen per cent of the alloy. This alloy could be filed rather readily, and could be worked cold into rods and sheets if sufficient care was exercised.

I next produced an alloy of cobalt with chromium in the same manner, but when the reaction took place a certain amount of free oxygen was evolved, and the metal was thrown from the crucible. This was due to the fact that the higher oxide of cobalt ($Co_2O_3$) was used,

* A paper presented at the American Electrochemical Society in Boston, April 9, 1920, reprinted from *Transactions of the American Electrochemical Society*, 1920, Vol. xxxvii.

while in the former experiment NiO was employed.

The reaction for the production of the nickel alloy was as follows: :—

$$3NiO+Cr_2O_3+2Al_2=Ni_3Cr_2+2Al_2O_3.$$

The reaction in the case of cobalt was :—

$$2Co_2O_3+Cr_2O_3+3Al_2=Co_4Cr_2+3Al_2O_3.$$

It is obvious that by varying the proportions of the various oxides, alloys of varying compositions can be obtained.

It was only a step from this reaction to the production of the alloy by the simultaneous reduction of the oxides of their constituent metals by means of carbon.

Afterwards, they were produced on a commercial scale by melting pure nickel or pure cobalt with chromium. Since the cobalt-chromium alloys possessed great hardness and could be worked at a bright red heat, it seemed to be the more promising field for further investigation, and when, in the early part of 1900, large quantities of cobalt ore were discovered in Canada, and it became possible to procure the cobalt oxide at a comparatively reasonable price, I decided to place the alloy on a commercial basis.

The discovery of these alloys was first made public at a meeting of the American Chemical Society, in San Francisco, in 1910.

About this time I discovered that by adding tungsten or molybdenum to the cobalt-chromium alloy, its hardness could be very much increased, though the addition of either of these metals in any considerable quantity rendered the alloy unworkable either hot or cold. It could, however, be cast into almost any desired form, and when cast bars were ground to a cutting edge and placed in the tool-holder of a lathe, the alloy at once showed a considerable advantage over high-speed steel as a lathe tool.

The first remarkable test of this sort was made in the machine shop of the Haynes Automobile Company. A large boring mill had been purchased for boring cylinders. This mill was supplied with a boring head in which were inserted small radial cutters which bored out the interior of the cylinders directly from the rough castings. I was informed by our superintendent that he had found it impossible to work the mill to more than half its rated capacity on account of "burning" the steel tools. We had up to that time made only a few tests on the lathe of Stellite tools, but he was very anxious to try the alloy in the form of boring cutters. I accordingly produced a set of cutters of Stellite, which were inserted into the boring head. When I came to the factory the next day, about 11 30 in the forenoon, I asked the man at the mill what success he had achieved, and he replied that he "had a day's work out at twenty minutes of eleven in the forenoon." In fact, he was boring more than twice as many cylinders in a day with Stellite tools as could possibly be bored with steel ones. This test fully demonstrated the practical utility of Stellite tools.

In 1912, another paper was read on this alloy in New York, at one of the sessions of the International Congress of Applied Chemistry.

It was found quite difficult to make metal of uniform texture and quality in the form of castings, but most of the difficulties have been overcome, and we are now placing upon the market cast tools of various kinds made of Stellite, which are of standard quality both as to strength and hardness.

The alloys are made almost entirely in electric furnaces of the Snyder type. The materials composing the alloy are placed in the furnace in the usual manner, and the current turned on. The alloy fuses rapidly, without much oxidation, under the intense heat of the electric arc. We find that of the metals composing the alloy, chromium is most readily oxidised, while cobalt seems to show more volatilisation, and tungsten is subject to the least change. It is true that the portion of furnace above the metal becomes filled with nearly pure carbon monoxide. This gas will oxidise chromium under certain circumstances at very high temperatures, though apparently no free carbon is produced in the furnace. This is probably because there is sufficient free oxygen or carbon dioxide to re-oxidise any carbon that may be temporarily produced.

At first much difficulty was experienced with the electric furnace linings, but after a certain amount of experimental work we were able to produce a magnesite lining which gives most excellent satisfaction in practice. When we first began the use of these furnaces, we considered ourselves fortunate if we could get eight or ten melts without either complete re-lining or heavy repairs. We now commonly obtain from two thousand to three thousand melts from a single lining, and some of them stand even higher than this.

The electric arc, on account of its extremely high temperature, causes a certain amount of volatilisation, or oxidation in the melting of many metals, but Stellite withstands the conditions remarkably well, particularly after the fusion is once made. In melting scrap, however, if certain precautions are observed, only a very slight loss is experienced in re-melting. Stellite can be melted in covered crucibles under suitable precautions with a loss of less than 2 per cent, and sometimes it does not even reach 1 per cent.

Not only have the Stellite alloys containing cobalt, chromium, and tungsten, or cobalt, chromium, and molybdenum shown great economic advantage as lathe tools, but the binary alloys (consisting of cobalt and chromium only) have likewise received a wide application in the form of dental instruments, surgical instruments, pocket knives, &c.

A modified Stellite alloy, known as Festel metal, consisting of cobalt, iron, and chromium, is also manufactured into table knives, which give excellent results in service.

All of the above alloys are practically immune to all atmospheric conditions, whether the air be moist or dry, or whether it contain minute quantities of sodium chloride or sulphuretted hydrogen. Knives made of this alloy can be used for cutting all sorts of fruit, including lemons, oranges, apples, &c., without becoming discoloured in the slightest degree. A new and interesting application of malleable Stellite is as a substitute for gold in the manufacture of pen points for fountain pens. The tips of these pens may, if desired, be made of extremely hard Stellite, which can be welded to the malleable alloy. This application is particularly gratifying because the metals replaced, gold and irrodosmium, are exceedingly expensive.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

*November* 17, 1921.

Prof. C. S. SHERRINGTON, President, in the Chair.

THE following papers were read:—

*"The Design of Repeating Patterns."* By Major P. A. MACMAHON, F.R.S., and W. P. D. MACMAHON.

The object of the paper is to provide a method for the study and classification of repeating patterns in space of two dimensions. It is founded upon the simplest geometrical forms which happen to be repeats. These are employed as bases and are subjected to specified transformations which depend upon certain contact systems between the sides which are in contact in the assemblage. The classification is based upon:—

(i) The base polygon;
(ii) The general contact system;
(iii) A subdivision of the contact system (ii).

Particular attention is paid to the design of symmetrcal repeats, and a calculus, with this object in view, is introduced. This involves a further sub-division of (iii) above into genera, each of which includes an infinite number of repeats. The symmetrical repeats based upon the equilateral triangle and upon the square involve 51 and 27 genera respectively.

Repeats themselves are of three varieties—the block, the "stencil," and the "archipelago"—the nomenclature of the last two being adopted at the suggestion of Mr. G. T. Bennett. There is a further broad division into normal and abnormal repeats.

A theory of "complementary repeats" is established and is believed to be of significance and importance It is shown that a contour can be drawn around every normal repeat in an infinite number of ways, in such wise that the area within the contour, which does not belong to the repeat, is itself a repeat. The contour referred to, under specified conditions which can be determined, is itself the boundary of a repeat, which is therefore a combination of the original repeat and its complementary.

Repeats with circular boundaries (of the "stencil" variety) are brought forward and illustrated. By permission of Mr. Bennett, occasion is taken to announce his discovery of the fact that "every quadrilateral figure" is a repeat.

*"A Problem in the Theory of Heat Conduction"* By Prof. J. W. NICHOLSON, F.R.S.

The main problem is that of the conduction of heat outside a cylinder whose surface is maintained, from some specified instant, at a constant temperature for all subsequent time A solution is obtained for the temperature at any point in the external medium, and for the rate of loss of heat from the cylinder at any instant. The principle of the method is the use of a generalised form of the Bessel-Fourier double integral. Subsequently a solution is obtained, in a similar way, for the general problem in which the temperature maintained on the cylindrical surface is not constant, but any arbitrary function of time.

*"The Thermal Stresses in Spherical Shells Concentrically Heated."* By Prof. C H LEES, D.Sc., F.R.S.

It is shown in this paper that the thermal stresses in the material of a furnace of approximate spherical form due to differences of temperature, and the stresses due to pressures on the inside and outside surfaces, may be expressed in simple form in terms of the volume of the spherical surface through any point or of its reciprocal. It is then shown that the expressions lend themselves readily to geographical representation, and lead to graphical methods of treating the whole problem. The elastic constants of the material have to be taken as constant, but it is shown how the variation of the dilatation with temperature may be taken into account.

The numerical values of the stresses in a furnace of fire-brick, with walls 20 cms. thick, whose surfaces are at 1100° C. and 100° C. respectively, are calculated, so far as they can be, with the constants available for fire-brick. The increase of stress due to sudden changes of temperature of the inside surface is discussed.

*"Mathematical Foundations of Theoretical Statistics."* By R. A FISHER.

Methods of reduction of data implicitly involve interpretation of data to be handled as a random sample of some hypothetical infinite population, the parameters of which it is desired to estimate. In this process three types of problem arise: (*a*) to determine mathematical specification of population from which sample is regarded as drawn; (*b*) to estimate from sample the parameters of population; (*c*) to calculate distribution of statistics calculated from random samples.

The paper deals mainly with problems of estimation (*b*). Two criteria of adequacy of any particular method of estimation have hitherto been put forward: (1) the Criterion of Consistency merely requires that the method when applied to the whole population should yield the required parameter; (2) the Criterion of Efficiency compares the value of different statistics, suggested as estimates for a given parameter, by means of standard deviations of statistics from large samples.

The most efficient statistic is that which has least standard deviation; the efficiency of any other statistic is the ratio of number of observations required by most efficient statistic to that required by statistic under consideration in order to obtain a value of same accuracy.

It is shown that Criterion of Consistency is a special case of Criterion of Sufficiency, which requires that the sufficient statistic shall include the whole relevant information provided by sample. Efficiency of any other statistic may be looked upon as percentage of relevant information available and utilised by that statistic.

Proof is given that a certain class of statistic (those obtained by method of maximum likelihood) are always sufficient statistics, and therefore have least possible probable error. The standard deviation of these statistics being easily calculated, the efficiency of any other statistic, of known probable error, may be found.

*"The Diffraction of Plane Electromagnetic Waves of a Perfectly Reflecting Sphere."* By F. P White.

This paper is an attempt to obtain from the well-known series solution for the problem of the diffraction of plane electromagnetic waves by a perfectly reflecting sphere approximations which are suitable for numerical evaluation when the radius of the sphere is large compared with the wave-length.

The method employed consists in transforming the series into a contour integral along a path of "steepest descents" and then approximating to the value of this integral For points which are not nearly directly behind the sphere, the first approximation obtained agrees with that found by Dr. Bromwich (*Phil. Trans.*, A, 1920, ccxx., 196); second approximations are also obtained, which agree fairly well with the numerical results of Messrs. Proudman, Doodson, and Kennedy (*Phil. Trans.*, A, 1917, ccxvii., 279), for the case $\kappa a = 10$, $a$ being the radius of the sphere and $2\pi/\kappa$ the wave-length.

The more difficult region behind the sphere is also investigated by a similar method, the integrals involved being here much more complicated, and the results are again compared with those of Proudman, Doodson, and Kennedy.

*"Whispering Gallery Phenomenon."* By C V. Raman and G. A. Sutherland.

The paper deals with some observations made in the Whispering Gallery at St. Paul's Cathedral and also in the laboratory experiments, which show that, while Rayleigh's theory of the phenomenon is undoubtedly on the right lines, it does not offer a complete explanation of all that is observed. The optical analogue of the Whispering Gallery is described, and it is shown that the effect contemplated by Rayleigh, that is, a single belt of maximum intensity close to the wall, is obtained only in the limiting case when the radius of the reflecting circle is practically infinite in comparison with the wave-length. For more moderate values of the radius of curvature. we get a succession of belts of alternately great and small intensity. Similar effects are also observed in the acoustical case. The explanation of the results is discussed, and it is shown that the slight inevitable deviation from the condition of strictly circumferential wave-propagation postulated by Rayleigh must give rise to such effects.

## SOCIETY OF GLASS TECHNOLOGY

A meeting of the Society of Glass Technology was held in the Fuel Department, the University, Leeds, on Wednesday, November 16, 1921, the President, Dr. Morris W. Travers, F.R.S., in the Chair.

Following a demonstration by Mr. F. W. Knowles of an "Improved Gas Reversing Valve for Regenerative Furnaces", the meeting resolved itself into a discussion of problems connected with "The Melting of Glass".

A lively discussion took place upon various questions connected with the technique of glass-making. The President then announced that the next meeting would be held in London on December 14, 1921, and that by the courtesy of the Directors a visit had been raranged for the forenoon of that day to the works of Messrs United Glass Bottle Manufacturers, Ltd., at Charlton.

## NOTES.

Commercial Research Fellowships. — The Executive Council of the British Empire Exhibition announce five or more Commercial Research Fellowships for competition among Chambers of Commerce in the United Kingdom. The value of each Fellowship will be not less than £500, and will include a rst-class return ticket to the Dominion, Crown Colony, &c., to which the Fellow will proceed. The subjects of research will be as follows: (1) The best means of promoting inter-imperial trade in a selected staple industry; (2) The methods whereby the British Empire Exhibition can further the interests of this trade; (3) The potential resources in raw materials, &c., in the Dominion or Crown Colony visited, and the best means for exploiting these in the mutual interest of the Dominion and this country; (4) The means whereby these undeveloped resources may be adequately represented at the British Empire Exhibition and brought to the attention of interested financial or industrial groups. Particulars of conditions can be obtained by application to the Secretary, British Exhibition (1923) Incorporated, 16, Hobart Place, London, S.W.1.

Institution of Rubber Industry.—Meetings will be held monthly at London and each of the following centres: Manchester, Birmingham, and Glasgow. Papers of practical interest to all sections of the rubber industry will be read at these meetings on dates to be announced later, as follows: "Ingredients of Rubber Mixings," by Dr. Samuel S. Pickles, D.Sc.; "Widening the Field for Rubber Manufactures," by Fordyce Jones (Chairman, Reliance Rubber Co. Ltd.); "Vulcanisation—Past, Present, and Future," by Dr. Schidrowitz, Ph.D., F C.S.; "Rubber Works' Worries," By Capt. F. J. S. Gray (Works Manager, S Helens Cable & Rubber Co. Ltd.); "Cold Vulcanisation," by S. J. Peachey (The Peachey Process Co Ltd.); "Rubber Pigments—Composition and Stability under Cure," by H. Dudley Ward; "Difficulties in Rubber Manufacture," by Dr. J. Torrey (Vice-President North-Western Rubber Co.); "Crude Rubber from the Consumers' Standpoint," by Dr. W. C. Geer (Vice-President, The B. F. Goodrich Co.); "Rubber Mixes and the Question of Accelerators," by J. L Rosenbaum (Hooley Hill Rubber and Chemical Co.); "Rubber Production"; "Troubles in Rubber Works"; "Rubber Proofing"; Special Rubber Machinery"; Electricity and its Uses in the Rubber Industry"; "Tyres—Solid and Pneumatic"; "Golf Ball Manufacture"; &c.

Appointment.—The Chancellor and Trustees of the University of Pittsburgh announce the appointment of Edward Ray Weidlein as Director of the Mellon Institute of Industrial Research.

Celluloid —In view of the increasing use of celluloid for industrial purposes and of its inflammable nature, many attempts have been made to produce a material that while possessing the valuable properties of celluloid shall be free from

fire risk. A new manufacture has been placed upon the market under the name of "Celastoid," which is claimed to have "all the good qualities of celluloid and none of the bad ones." Celastoid, or cellulose-acetate, can be obtained from the British Cellulose & Chemical Manufacturing Co., 8, Waterloo Place, London, S.W.

The Making of Reflecting Surfaces.—Discussion at a Joint Meeting of the Physical and Optical Societies held on November 26, 1920, at the Imperial College of Science and Technology, South Kensington, S.W.7.—We have received from the Hon. Secretary (Papers) of the Optical Society, a copy of the Proceedings of this important discussion. The work opens with a survey of the Bibliography of Metallic Deposition on Glass, and of the more important papers on the Construction and Nature of Reflecting Surfaces, by R. Kanthack. The outcome of the Authors' interesting and exhaustive survey is that the fundamental discovery of a process for depositing silver upon a glass surface is due to Liebig, who, in 1853 published in the *Ann d. Pharm.* a method for depositing silver upon glass in the form of a brilliant mirror, by the action of aldehyde upon silver oxide in water. Since then, although very numerous papers have appeared upon the subject, very little real progress has been made, and the author concludes his survey by stating that "at the present time—85 years after Liebig's classical discovery—we have not evolved any method of chemical deposition on glass so scientific and practically perfect that it could be adopted officially." Then follows a list of the more important papers on the construction of reflecting surfaces commencing with a paper by S. Bernard, appearing in the *Jour. de l'Ecole Polytechnique*, Paris, in 1798, down to that of A. Silvermann and F. D. Neckermann that was published in the *Trans. Am. Chem. Soc.* in 1915. After this introductory survey, the following papers and discussions appear: Survey of the Bibliography of Metallic Deposition on Glass, by R. Kanthack; A Bibliography of the more important Papers on the Construction and Nature of Reflecting Surfaces, by R. Kanthack; Notes on the Formaldehyde Process of Silvering, by H. N. Irving; Some Workshop Notes on Silvering, by Sir James Weir French, D.Sc. (Messrs. Barr & Stroud, Ltd., Glasgow); The Silvering of Glass Reflectors by Chemical Deposition, by F. Ellerman and H. D. Babcock (Mount Wilson Observatory); The Silvering of a Large Reflector, by C. R Davidson (Royal Observatory, Greenwich); Note on the Silvering of Quartz and Glass Fibres, by R. S. Whipple, M.I.E.E. (The Cambridge and Paul Instrument Co. Ltd.); Some Notes on Mirrors used for Reflecting Heat Radiation, by Prof. Chas. Féry (Ecole Municipale de Physique et de Chimie, Paris); Deposition of Metals by Cathodic Spluttering in Vacuo, by F. Ellerman and H. D. Babcock (Mount Wilson Observatory); Note on the Production of Mirrors by Cathodic Bombardment, by F. Simeon, B.Sc., F.Inst.P. (Messrs. Adam Hilger, Ltd.); Platinum Reflecting Surfaces Prepared by the "Burning-in" Process, by Julius Rheinberg, F.R.M.S., F R.P.S.; A Note on Mirrors for use in Optical Instruments under Industrial Conditions, by W. G. Collins (The Cambridge and Paul Instrument Co. Ltd.); A Photometric Method of Measuring the Reflecting Power of Mirrors, by John W. T. Walsh, M.A., M.Sc. (The National Physical Laboratory); General Discussion. The work, which is well printed and illustrated, is published by the Fleetway Press, Ltd., Dane Street, Holborn, W.C.1, price 5s. (postage 3d.).

Tenders for Trade Ship.—The Directors of the British Trade Ship, of which Earl Grey is Chairman, announce that provisional tenders are being obtained by the builders of the ship for the various parts and fittings. Exhibitors who are in a position to supply some part or fitting as an exhibit actually in use on board, quite apart from their display in the Exhibition proper, are naturally anxious to have their products accepted for this purpose. At Wallsend-on-Tyne, where the ship will be built, and at the offices of the British Trade Ship, 12, Grosvenor Gardens, London, the examination of specifications is taking place with a view to determining the market value of each part and its exhibition value to the supplier. The examination is of considerable interest as revealing the place of different cities in the construction and equipment of the Trade Ship. Birmingham wants its bedsteads in the best cabins, Kidderminster its carpets, Bradford its textiles, not only on show, but in use; Sheffield its cutlery, and so on with hardware, machinery, leather, glass, and electrical goods. The trades mentioned make up two-thirds of the total exports of the country, and the realisation of this fact explains why the Directors of the Trade Ship are inundated with demands to provide exhibits which will be actual fittings of the ship. The acid test which the builders will apply in all cases is that of quality, and, unless an exhibitor can satisfy them that his product is of the highest quality, it will not be included as part of the structure or of the fittings of the ship. When full arrangements have been completed, the names of the chief firms responsible for the various component parts of the Trade Ship will be published. The Trade Ship *British Industry* will go on its voyage as the representative of the manufactures of many cities.

British Trade with France.—In order to assist in the stimulation of British trade with France, the British Chamber of Commerce in Paris is preparing a new and revised edition of its Franco-British Trade Index. The cost of compilation, classification, printing, and distribution of the Trade Index amongst French buyers will be met from the funds of the Chamber, the only stipulation being that the firms appearing therein, under the various classified headings of their manufactures or exports, shall have shown their interest in British Trade in France by becoming members of the Chamber. No subsidy is received by the Chamber from the Government, which entirely depends on the members' subscriptions to carry on its valuable work. The membership roll at present includes nearly 2000 British firms or subjects. Supplies of forms of application for membership and forms of insertions for the Trade Index, for distribution to business friends, may be obtained on request to the Secretary of the British Chamber of Commerce, 6, rue Halévy, Paris.—*Board of Trade Journal*, November 10, 1921.

NATIONAL CERTIFICATES IN CHEMISTRY TO STUDENTS IN TECHNICAL SCHOOLS AND COLLEGES IN ENGLAND AND WALES.—The Institute of Chemistry is undertaking the functions assigned to it in these Rules at the invitation of the Board of Education, and full particulars for the award of certificates can be obtained by application to H.M Stationery Office, Imperial House, Kingsway, W.C.2, price 2d., or through any bookseller.

THE Council of the Institution of Electrical Engineers have elected as an Honorary Member Lord Southborough, P.C., G.C.M.G., &c., who was formerly Sir Francis Hopwood, and had a distinguished career at the Board of Trade and other Government Departments.

## NEW COMPANIES.

The under-mentioned particulars of New Companies recently registered are taken from the Daily Register compiled by JORDAN & SONS, LIMITED, Company Registration Agents, Chancery Lane, W.C.2.

RIDING'S CASH DRUG STORES, LIMITED.—(177736)—Registered November 9th, 1921. 9, Wickham Lane, High Street, Plumstead To acquire and carry on the business of Chemist, Druggist and Drug Stores. Nominal Capital: £1,200 in 1,200 Ordinary Shares of £1 each. Directors: W. E. Hallock, 9, Wickham Lane, Plumstead S.E.18; (Mrs.) Emily Hallock, 9, Wickham Lane, Plumstead, S.E.18.

ALFRED BOND, LIMITED.—(177711)—Registered November 8th 1921. To acquire and carry on the business of Chemists and Drug gists Nominal Capital: £16,000 in 16,000 Shares of £1 each Directors: A. Bond, 45, Bank Street, Newquay, C. E. Whetford Rosemellny, St. Columb; M. Gatley, Fore Street, St. Columb Qualification of Directors: 250 Shares. Remuneration of Directors £150 to be divided.

POMMEROLS CURE, LIMITED.—(177899)—Registered November 18th, 1921. 72-74, Victoria Street, Westminster, S.W.1. To carry on the business of Chemists and Druggists. Nominal Capital £2,000 in 2,000 Ordinary Shares of £1 each Directors: J. G. L. Pommerol, 27, Richmond Road, Bayswater, W.2, E. H. Hove White Cottage, Wargrave, Berks.; F. Hill, Vaughan Lodge, Long Ditton, Surrey; J. Molendri, 53, James Street, Cardiff Qualification of Directors: 1 Share Remuneration of Directors: To be voted by Company in General Meeting

## New Patents.

THIS List is specially compiled for the *Chemical News* by Messrs Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, W.C.2, from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

29198—Briggs, A.—Treatment of iron liquors containing zinc an sulphate of soda. November 3

29137—British Cellulose & Chemical Manufacturing Co. Limited.—Treatment of cellulose derivatives. November 2

29289—British Dyestuffs Corporation, Ltd.—Manufacture of phenyl glycine or compounds thereof November 3

29902—British Dyestuffs Corporation, Ltd.—Mono-nitro and monoamino derivatives of P-halogenated dialkylanilines November 9

30119—Chemicals & By-Products, Ltd.—Indicator for determining weak acids or bases in the presence of strong acids and bases, etc. November 11

30005—Air Liquide Soc Anon pour l'Etude et l'Exploitation des Procedes G.—Apparatus for synthesis of ammonia. November 10

30089—Whyte, D—Process for conversion of sulphite of lead water paste into oil paste. November 11

*Specification published this Week.*

170613—South Metropolitan Gas Co., and Parrish P.—Manufacture of ammonium sulphate

*Abstract Published this Week*

*Synthetic Resins*—Patent No. 16934.—A method of producing Synthetic Resins has been Patented by Mr. H. V Potter and W. F. Fleet, 98, Bradford Street, Birmingham, and Damard Lacquer Co. Ltd., 82, Victoria Street, Westminster, Phenol or its homologues when condensed with acetaldehyde or its polymers produces a resin which is soluble and does not harden on heating. Formaldehyde or its polymers may be added at any stage of the process to render the product less soluble or insoluble or to make it harden. Acids, bases and salts may be used as accelerators, the following being mentioned as suitable, namely sulphuric acid, ammonia, caustic-alkali, oxalic acid and phenyl hydrazine hydro-chloric.

*Nickel, Sodium Salts.*—Patent No. 169247.—A process for obtaining Sodium Salts has been Patented by Mr. E E. Naef, 16, Loughborough Road, West Bridgford, Nottingham. Finely divided nickel sulphide is heated with solid caustic soda, or with a mixture of caustic soda and sodium carbonate, common salt, sodium sulphate, sodium sulphide, or lime, and with or without the addition of powdered coal The operation may be carried out in an atmosphere of hydrogen or gases containing hydrogen. Sulphides, hydrosulphides, and thiosulphates of sodium are formed and metallic nickel is precipitated, which, after slight reduction in hydrogen is applicable as a catalyst in processes for the hydrogeneration of oils. The molten salts may be poured off, or the whole mass may be treated with water to dissolve the salts. The nickel may be refined electrolytically or by a carbonyl process, or converted into sulphate.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

## MEETINGS FOR THE WEEK

*Monday, December 5.*

Royal Society of Arts, 8.—(Cantor Lecture) "Processes of Engraving and Etching" by Arthur M. Hind.

Institute of Electrical Engineers, 7. Discussion on "Some Recent Developments in the Design of A.C. Instruments".

*Tuesday, December 6.*

Royal Society of Arts, 4.30 "British Columbia" by Frederick C. Wade.

*Wednesday, December 7.*

Royal Society of Arts, 8. "Literature and International Relations" by Emil Cammaerts

Society of Public Analysts, 8 "Estimation of small quantities of Antimony in Copper and Brass" by B. S. Evans. "The Inks of Ancient and Modern Egypt" by A. Lucas. "Analysis and Use of Red Squill in Rat Poisons" by C L. Claremont

Institution of Electrical Engineers, 6 An Investigation of Transmitting Aerial Resistances" by T. L. Eckersley.

*Thursday, December 8.*

Royal Society "A Study of the Glow of Phosphorus. Periodic Luminosity and Action of Inhibiting Substances" by Lord Rayleigh. "The Aurora Line in the Spectrum of the Night Sky" by Lord Rayleigh "The Energy in Air, Steam, and Carbon Dioxide from 100°C. to 2,000°C." by W. D. Womersley. "Atmospheric Pressure and Refractive Indices with a corresponding Table of Indices of Optical Glass" by Lt. Col. J. W. Gifford. "A new Form of Interferometer" by H. P. Waran. "Viscosities of the Hydrogen Halides" by H. Harle.

Chemical Society, 8. "The Genesis of Ores" by Professor J. W Gregory.

# NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemical Apparatus, &c., for review or notice to be addressed to the EDITOR.

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## ADVERTISEMENTS.

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THE CHEMICAL NEWS.
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## THE PRESENT POSITION OF THE THEORY OF DESCENT, IN RELATION TO THE EARLY HISTORY OF PLANTS.*

By H. D. SCOTT, LL.D., F.R.S.

(Concluded from page 293.)

THERE is one more point in connection with the Rhynie plants which may be mentioned, as it is of purely morphological interest, and may be more in place here than at a later stage of the discussion.

In *Hornea*, as Kidston and Lang have shown, the terminal "sporangia evidently arose by the transformation of the tips of certain branches of the plant."

They are, in fact, very little modified as compared with vegetative parts of the stem. The epidermis and subjacent layers of the sporangial wall differ but slightly from the corresponding tissues of the branch, while the columella is continuous with the phloem, and resembles it in structure. The sporangium has no special stalk, and in some cases is forked, like the stem, having evidently been formed when the branch was in the act of dichotomy.

In *Rhynia* the sporangia are better differentiated, but here also cases occur where the spore-bearing region differs little in structure from the branch which it terminates. In both genera the spore-containing organ is thus nothing but the more or less altered end of a branch, quite comparable to the stichidium, which is differentiated in some Red Seaweeds as the receptacle of the tetraspores, while in other Algæ of this group the tetraspores are produced in unaltered portions of the thallus. In *Hornea* the fertile branch-ending is less differentiated than in *Rhynia*, and we must be prepared to meet with related forms in which the spore-bearing region was not differentiated at all, except for the presence of the spores.

Goebel taught that the sporangium was an organ *sui generis*, a special reproductive structure, which had never arisen from any vegetative part of the plant ("Vergleichende Entwickelungs-geschichte der Pflanzenorgane." Schenk's "Handbuch der Botanik," Bd. III., Part I., 1884, p. 130). His view has been generally accepted, but, in the light of the conditions in Rhyniaceæ, appears to be no longer tenable. While the spores may still be described as organs *sui generis*, for there have always been reproductive cells since plants became multi-cellular, the sporangium proves to be really a portion of the vegetative stem or thallus, which has gradually become specialised as a receptacle for the spores. The sporangium thus turns out to be strictly homologous with a definite part of the vegetative body of the plant. In these remarks I am glad to find myself entirely in accord with the views of Kidston and Lang, as stated in their fourth memoir on the Rhynie plants.

The recent work on the Early Devonian Flora has wide bearings. It has long been noticed that among the fossils of that period no typical Fern-fronds are found. Those remains which are most suggestive of Fern-like habit consist merely of a naked-branched rachis. It used to be assumed that the absence of a lamina might be explained by bad preservation. But, as Prof. Halle points out, the chief reason for condemning the preservation as bad was the fact that a lamina was absent!

The evidence really seems to indicate that the so-called fronds of that age did not possess a leaf-blade. As Prof. Halle says: "In the Lower Devonian, finally, we find frond-like structures bearing sporangia, but no fronds with developed laminæ. One can hardly escape the conclusion that the 'modified' fertile fronds may represent the primitive state in this case, and that the flattened pinnules are a later development, as suggested by Prof. Lignier" (T. G. Halle, "Lower Devonian Plants, from Röragen, in Norway." Stockholm, 1916, p. 38). These naked fronds may, in fact, be regarded as the little-differentiated branches of a thallus. It is often impossible to say whether we have to do with the ramification of a stem or with a frond, Halle even suggests that one of his species of *Psilophyton*, *P. Goldschmidtii*, may furnish us with an intermediate stage between the two, as required by Lignier's hypothesis. Plants of the *Rhynia* type may represent a still earlier phase, in which there was no differentiation whatever, but merely a branched thallus. It is a curious point that "the circinate vernation of the Fern-fronds is paralleled in the branches of *Psilophyton princeps*.

The evidence, as at present understood, seems to suggest that, in the earlier Devonian flora, Ferns, properly so called, may not yet have been in existence. The predecessors of the Ferns (Lignier's "Primofilicinées," *not* Arber's "Primofilices") were there no doubt, but not, so far as we know, the Ferns themselves. Yet it seems that highly organised stems of a Gymnospermous type were already present at about the same period. Thus the evidence from the older Devonian Flora, so far as it goes, materially supports the opinion that the Seed Plants cannot have arisen from Ferns, for the line of the Spermophyta seems to have been already distinct at a time when true Ferns had not yet appeared.

The idea that the Gymnosperms were derived, through the Pteridosperms, from the Ferns, which I once advocated, must, I think, be given up, on grounds which were stated two years ago at the Bournemouth meeting of the Association. It is safer to regard the Pteridosperms, and therefore the Seed Plants generally, as a distinct stock, probably as ancient as any of the recognised phyla of Vascular Cryptogams, and derived from some unknown and older source. At the same time the striking parallelism between the Pteridosperms and the true Ferns must be recognised. These views are essentially in agreement with those previously expressed by my friend Dr. Kidston.

I may be permitted to quote in this connection an interesting remark made by Prof. Paul Bertrand in a letter received last year. He was speaking of a strange group of plants of Lower Carboniferous or possibly Upper Devonian age, the Cladoxyleæ. These plants have a complex

*Address delivered before Section K, British Association (Edinburgh Meeting).

polystelic structure in both stem and petiole, but seem to be quite distinct from the later and better-known polystelic family, Medulloseæ. Prof. Bertrand, the chief living authority on the Cladoxyleæ, speaks of them as very primitive types, in which the distinction between stem and petiole was still but little marked. Yet he considers them as most probably Phanerogams. These views, if confirmed, imply that the Phanerogams or Seed Plants started as a distinct phylum, quite low down, at a phase when the differentiation between stem and leaf was still incomplete.

Without laying too much stress on an expression of opinion such as Prof. Bertrand's, I believe the present evidence is in harmony with the view he suggests. The Spermophytes, as it seems, have been an independent class of plants from very early times; they are not to be derived from the Vascular Cryptogams, as we have hitherto conceived them, but are of the same standing with them, having sprung from some long-extinct stock, comparable, perhaps, to Kidston's and Lang's Psilophytales, though not necessarily on the same line.

The significance of the Pteridosperms has perhaps been somewhat misunderstood. It now seems that they do not, as some of us once imagined, indicate the descent of the Seed Plants from Ferns, but rather show that the Seed Plants passed through a Fern-like phase; they ran a parallel course with the true cryptogamic Ferns, and, like them, sprang from some quite early race of land plants, such as Rhynie has revealed to us. But the phylum was never any more Fern-like than the Pteridosperms themselves. This, at least, is the view which now suggests itself, but our knowledge is still very meagre. We especially want to know more about the Devonian Spermophyta, for at present we have scarcely any evidence even of the existence of seeds in any Devonian Flora. Such data as we possess are all anatomical, and a disciple of Williamson must be on his guard against the risk of repeating the old mistake of the Brongniartian school.

Having ventured so far into speculative regions, it may be well to return for a moment to the facts, and ask to what extent our knowledge of the Fern-like Seed Plants has advanced since the original discoveries of 1903-1906. I fear that there is not very much to record. We now have one or two additional species of *Neuropteris* bearing seeds, and also the probable seed of *Heterangium*. Further, we have various indications of the characters of the pollen-bearing organs in some Pteridosperm genera, though the documents, being mostly in the form of impressions, are deficient in detail. Such new information as has come to hand confirms in a satisfactory manner our former conclusions, but does little to extend them.

On the anatomical side there has been more liveliness. We now know quite a number of Palæozoic plants, of varied structure, which have something in common with the better-established Pteridosperm families, Lyginopterideæ and Medulloseæ, while they certainly have nothing to do with Lycopods, Horsetails, or Sphenophylls. We therefore call them Cycadofilices or Pteridosperms. I prefer to use one name for them all and incline to the latter, for, while the plants are more or less Fern-like in structure, many of them show no special resemblance to Cycads.

At present we know of no fewer than eight families, based mainly on anatomical characters, which we provisionally include under Pteridosperms:—

1. The familiar Lyginopterideæ (Lower and Upper Carboniferous).
2. The *Rhetinangium* family, founded on Dr. Gordon's new genus (Lower Carboniferous).
3. The Megaloxyleæ, discovered by Prof. Seward (Upper Carboniferous).
4. The Calamopityeæ, recently enriched by Dr. Kidston with a new genus, besides new species (Lower Carboniferous).
5. The *Stenomyelon* family, another of Dr. Kidston's discoveries, described by him in conjunction with Gwynne-Vaughan (Lower Carboniferous).
6. The *Protopitys* type, a singularly isolated one, elucidated by Solms-Laubach (Lower Carboniferous). The above are all monostelic. Next come the two essentially polystelic groups:
7. Cladoxyleæ, already mentioned, a somewhat mysterious race, of Lower Carboniferous or possibly even Upper Devonian age.
8. The well-known Medulloseæ (Upper Carboniferous).

It is noticeable that five of these families are Lower Carboniferous (or possibly, in certain instances, older); one (Lyginopterideæ) includes both Lower and Upper Carboniferous members, while two (Megaloxyleæ and Medulloseæ) are at present known only from the Upper Carboniferous).

Of the eight families in question there are only two (Lyginopterideæ and Medulloseæ), in which we have any evidence as to the fructification. The other six are known only by their vegetative and mostly by their anatomical features. Of these, the Protopityeæ and the Cladoxyleæ are the most isolated, differing, for example, in the structure of their tracheides from the other families. There seems to be no reasonable doubt that the families represented by *Lyginopteris*, *Rhetinangium*, *Megaloxylon*, *Calamopitys*, *Stenomyelon*, and *Medullosa* are related, and belong to one and the same main phylum. Considering that members of two widely separated families in this series are known to have borne highly organised seeds, there is a strong presumption that the whole set were reproduced by seeds of some sort. In the case of the two families Protopityeæ and Cladoxyleæ the marks of affinity are less obvious, but even here there is more in common with the type-families Lyginopterideæ and Medulloseæ than with any other group.

I think then that we are justified, in the present very imperfect state of our knowledge, in provisionally keeping all these families together, as probably, in some wide sense, Pteridosperms. On this view, they formed a distinct, extensive, and varied class of plants, already very well developed in Lower Carboniferous times, and no doubt going back to the Upper Devonian, though here the available evidence is scanty.[1]

The question may be asked: Did all the Seed-plants pass through the Pteridosperm phase, or were there other parallel lines of descent? Some

recent work, no doubt, tends to link up the Cordaitales with the Pteridosperms. *Mesoxylon*, for example, is merely a *Cordaites* with centripetal wood in the stem, a character which strongly suggests an affinity with the *Lyginopteris* or *Calamopitys* type. In fact, some members of the Calamopityeæ (Zalessky's *Eristophyton*) show a certain approach to Cordaitales.

A more striking point is that no marked distinction has been found between the seeds of Pteridosperms and those of Cordaitales. The general community of seed-structure is strong evidence of close affinity and of a common stock.

There seems to be no proof that the family Cordaiteæ existed as such in Devonian times; we do not know much about them even in the Lower Carboniferous; the family is typically Upper Carboniferous and Permian. On the other hand, the *Pitys* family, which we include in the wider group Cordaitales, is as old as any known Pteridosperm; Zalessky's genus *Callixylon*, an evident ally of *Pitys*, is of Upper Devonian age. The affinities of the still more ancient *Palæopitys Milleri* have not yet been determined.

The position of the Pityeæ hangs in the balance, at least until Dr. Gordon's new results are fully placed before us. From his discovery of the peculiar foliage and leaf-traces as well as from the stem-structure it appears that the Pityeæ form a very distinct group, farther from the other Cordaitales than we at once supposed, and not much like any of the Pteridosperms either. At any rate, we may suppose that the Pityeæ branched off from the common stock low down while the Poroxyleæ and Cordaiteæ may have been of later origin. For the present, however, one may be content to regard the early Spermophytes as constituting a single main phylum. Since these words were written, however, Dr. Margaret Benson has maintained a contrary view, arguing that the Cordaitales, Ginkgoales, and Conifers represent a wholly distinct stock, more allied to the Sphenopsida than to the Fern-like races ("The Grouping of Vascular Plants," *New Phytologist*, June 30, 1921). The independence of this line has also been maintained by Prof. Chamberlain ("The Living Cycads and the Phylogeny of Seed Plants," *American Journal of Botany*, 1920, vii.) and discused by Prof. Sahni ("The Structure and Affinities of *Acmopyle Pancheri*," *Phil. Trans. R. Soc.*, Ser. B., 1920, ccx.).

On our hypothesis, the Upper Palæozoic phyla, with which we have to reckon, are the Pteridosperms (representing the early phase of the Seed-plants), the Ferns, the Sphenophylls, the Equisetales, and the Lycopods. These five lines were probably all well differentiated in the Upper Devonian Flora; the only doubt concerns the Equisetales, which seem not to be known with certainty before the Lower Carboniferous, but they were so well developed then that they must have existed earlier.

When we get back to the Middle and Lower Devonian the case is completely altered. Not one of the five phyla is here clearly represented, unless it be the Spermophyta; for these we have the evidence of apparently Gymnosperm-like stems. Thus the field is left absolutely open to speculation. We may imagine, either that the various phyla converged in some early vascular stock (illustrated by the Psilophytales), or that they ran back in parallel lines to independent origins among the transmigrant Algæ and, perhaps further still, to separate races of purely marine plants. Both views are represented in the publications of recent authors.

Dr. Arber, in his "Devonian Floras," maintained the early existence of three distinct lines of descent . the Sphenopsida, Pteropsida, and Lycopsida In agreement with the present writer, he included the Equisetales in the Sphenopsida. Each of the three lines is described as descended from Thallophytic Algæ of a distinct type. Thus Arber's view was decidedly polyphyletic. It must, however, be borne in mind that the supposed ancestral "Algæ" were plants in which he expected to find "some form of primitive vascular system, at least as far advanced as in *Psilophyton* (*l.c.* p. 74).

Arber derived the Spenopsida from Algæ-bearing whorled branches of limited growth, converted into leaves, which were originally and always microphyllous. The Pteropsida, with which he associated his Palæophyllales (*Psygmophyllum*, with foliage like the Maiden-hair tree), were descended from Algæ in which the branches were large, numerous, scattered, and not whorled, eventually metamorphosed to megaphyllous leaves. The Lycopsida, on the other hand, were derived from Algæ in which the usually dichotomous axis bore emergences, metamorphosed to microphyllous leaves.

Thus, as regards the origin of the leaf, Arber was in general agreement with Lignier, while he differed from the French author in the important point that he did not derive the Sphenopsida from the Fern-stock, but kept them as an independent line.

A remarkable feature in Arber's hypothesis is his treatment of the Psilotales. He made this problematic family "a quite independent race, also of Algal origin, which appeared on the scene long after the other races . . . possibly in Mesozoic times or even later" (p. 87). Thus he rejected both the connection with Psilophytales, suggested by Kidston and Lang, and the affinity with Sphenopsida, once maintained by the present writer.

We thus see that, on Arber's view, there were altogether four distinct lines of descent, running back independently to "Thallophytic Algæ."

Dr. Church, from a different point of view, arrives at somewhat similar conclusions, but he goes further. He says: "Speaking generally, it appears safer to regard a 'race' or 'phylum' as the expression of a group of organisms which derived their special attributes from the equipment of a preceding epoch, if not in one still further back. Thus all the main lines of what is now Land Flora must have been differentiated in the Benthic Epoch of the sea (*i.e.*, as Algal lines), as all Algal lines were differentiated in the Plankton phase. The possibility is not invalidated that existing groups of Land Flora may trace back their special line of progression to the flagellated life of the sea, wholly independently of one another (Pteridophyta)". ("Thalassiophyta," p. 41).

Taking the Lycopods and Ferns as an example, and arguing from their different types of flagellated spermatozoids, Dr. Church states: "It appears impossible to avoid the conclusion that

the Lycopod phyla only merge with those of the Filicineæ in a distant Plankton phase, even beyond an independent origin as benthic sea-weeds" (*l.c.*, p. 82). Thus the idea of independent parallel lines of descent is carried to its extreme limit. "Each phylum goes back the whole way, without any connection with anything else." Of course, this thorough-going polyphyletic conception is involved in the doctrine already mentioned —that morphological differentiation was attained in the sea before the transmigration.

I have cited Dr. Arber and Dr. Church as independent representatives, approaching the question from quite different sides, of the polyphyletic or parallel-phyla hypothesis. The opposite view, of convergent monophyletic races, is also well supported. Some reference has already been made to Prof. Halle's position. After speaking of the possible relation of the *Psilophyton* type to Lycopods on the one hand, and Ferns on the other, he adds: "From this point of view the whole pteridophytic stock would be monophyletic, the Lycopsida and the Pteropsida being derived from a common form already vascular. It would not thus be necessary to assume a parallel evolution of a similar vascular system along two different lines." (Halle, *l.c.*, p. 39).

He does not refer to the Articulatæ, of which, it is true, there are only the most doubtful indications in the Lower Devonian rocks. Halle, too, accepts Lignier's view of the two-fold origin of the leaf, from emergences in the Lycopsida, from thallus-branches in the Pteropsida.

Kidston and Lang, in the light of their Rhynie discoveries, regard Halle's survey as "a fair statement of the present bearing of the imperfectly known facts." They lay great stress on the synthetic nature of their genus *Asteroxylon*, which they say "appears to agree with *Psilophyton* in possessing in a generalised and archaic form characters that are definitely specialised in the Psilotales, Lycopodiales, and Filicales." They add: "The Geological age and succession of the Early Devonian plants, are, on the whole, consistent with the origin of the various groups of Vascular Cryptogams from a common source ("Old Red Sandstone Plants, showing structure, from the Rhynie Chert Bed," Part III., p. 673. In Part IV. this conclusion is further emphasised, and it is suggested that the Rhyniaceæ are really too simple morphologically to suit the views of either Lignier or Church). We have already referred to the Bryophytic features, which have been recognised in the Rhyniaceæ. Kidston and Lang make use of these to extend their tentative conclusions to the Bryophyta. In concluding their third memoir they say: "In *Rhynia* and *Hornea* we have revealed to us a much simpler type of Vascular Cryptogam than any with which we were previously acquainted. This type suggests the convergence of Pteridophyta and Bryophyta backwards to an Algal stock. The knowledge of *Asteroxylon* confirms and enriches our conception of a more complex but archaic type of the Vascular Cryptogams, which supports the idea of the divergence of the great classes of Pteridophyta from a common type, and links this on to the simpler Rhyniaceæ" (*l.c.*, p. 675). The monophyletic view, though stated with appropriate caution, could not be more clearly expressed. It is fully maintained in these authors' latter statements.

It is evidently impossible to decide between the two theories in the present state of our knowledge; we are now only beginning to acquire some conception of the vegetation of Early Devonian times. The discovery, however, of the existence at that period of an unexpectedly simple race of vascular plants to some extent favours a monophyletic interpretation, even though we accept with some reserve the wonderful synthesis of characters which *Asteroxylon* appears to exhibit. To some minds, too, the important points in which all existing Pteridophyta, however diverse, agree will still suggest a common origin not too remote. Among such common characters may be mentioned the alternation of generations with the sporophyte predominant; the development both of the spores and the sexual organs; and the histology, especially of the vascular system and the stomata. The community of reproductive phenomena is explained by Dr. Church on the principle that reproductive phases are inevitable, and are therefore the same in all phyla. A like explanation may to a certain extent be applicable to somatic features, some of which may be the necessary consequences of the sub-aerial transmigration. Thus a polyphyletic hypothesis may no doubt be justified, but it urgently needs to be supported by further evidence of the actual existence of separate stocks among the earliest available records of a Land Flora.

The study of Fossil Botany has led to results of the utmost importance, in widening our view of the Vegetable Kingdom and helping to complete the natural system, to use Solms-Laubach's old phrase once more. One need only mention the Mesozoic Cycadophytes, the Cordaitales, the Pteridosperms, the Palæozoic Lycopods and Equisetales, the Sphenophylls, and now, most striking of all, the Psilophytales, to recall how much has been gained. We have indeed a wealth of accumulated facts, but from the point of view of the Theory of Descent they raise more questions than they solve. In this address I have briefly touched on some of the most general and speculative problems in the hope of giving an opening for discussion. It might have been more profitable to deal in detail with definite facts of observation, but recent discoveries have brought us face to face with the great questions of descent among plants. However imperfect our data may be, both as regards the method and the course of evolution, the problems suggested, nevertheless, make urgent claims on our attention.

## HELIUM-BEARING NATURAL GAS.

By G SHERBURNE ROGERS.

### *Scope of the Investigation.*

THE gas helium, which was discovered on the earth by Sir William Ramsay in 1895 and which was at first regarded as one of the rare elements, was found in 1905 by H. P. Cady and D. F. McFarland to occur in small proportion in natural gas from many localities in Kansas. The announcement of this discovery excited interest in scientific circles, but as no practical use for helium was known it had no industrial value, and efforts were not made to extract it except in very small quantities for experimental use. During the first year of the World War, how-

ever, a British scientist conceived the idea of using helium instead of hydrogen for inflating balloons, and in 1915 a vigorous but unsuccessful search for the gas in England was begun under the direction Sir William Ramsay. This search was later extended to Canada, but without attaining satisfactory results On the entrance of the United States into the war the project was revived, and this Government undertook an energetic campaign for the production of helium in large quantities.

The value of helium for inflating balloons was brought to the attention of the Army and Navy by the Bureau of Mines, and that Bureau was commissioned to investigate the practicability of extracting the gas in large quantities and at a reasonable cost. When the technologic feasibility of the project was assured, the Geological Survey was called upon to investigate the helium resources of the country, in order to locate the richest supplies of the gas and to form estimates of the quantity available. This paper is based on the results of that investigation and describes the distribution and geologic relations of helium-bearing natural gas, making only brief mention of the technologic problems involved in the extraction and purification of the helium.

As the Survey's investigation was made strictly for military purposes it was necessarily directed toward locating an adequate supply of helium-bearing gas as speedily as possible, and practically no attention was given to the broader scientific problems involved in the origin or ultimate source of the helium. Considerable research will evidently be necessary before this problem can be successfully attacked, and in view of the probable development of commercial aircraft during the coming decade, and the probability that the cost of extracting helium from natural gas will be reduced sufficiently to permit its use in commercial balloons, it has been deemed desirable to present immediately a brief description of the chief sources of helium in the United States. At the same time the writer has endeavoured to describe the broader geologic relations of the helium-bearing gas, to discuss various theories of its origin, and to review the reported occurrences of helium in minerals and in other gases, in the hope that such a presentation of the problem will be of value to others who may later attempt to solve it.

*Value of Helium for Inflating Balloons.*

The value of helium for inflating balloons, especially airships of the Zeppelin type, lies in its lightness and its incombustibility. Hydrogen, the gas commonly used for inflating balloons, is the lightest substance known, but mixed with air it is explosively combustible. For this reason a balloon filled with hydrogen is very liable to be set afire, either by atmospheric electricity, by sparks from its power plant, or by any one of numerous accidents which may occur even when it is in its hangar. The fire hazard is, of course, greatly increased in balloons used for military purposes, a single incendiary bullet being usually sufficient to destroy a great airship; and this weakness, inherent in all hydrogen-filled balloons, was not only a potent factor in the practical failure of the German Zeppelin programme, but has always been a serious drawback to the development of lighter-than-air craft. On the other hand, Assistant Secretary of the Navy Roosevelt is authority for the statement: "With the fire risk eliminated the rigid airship or Zeppelin will hence be one of he most powerful weapons known (*Official Bulletin U.S.*, March 18, 1919, p. 9).

Helium weighs 0·0112lb. per cubic foot, and is thus twice as heavy as hydrogen, which weighs only 0·0056lb. per cubic foot. In comparison with air, however, both gases are so light that this difference is of small practical importance, and the lifting power or buoyancy of helium is 93 per cent of that of hydrogen. The slightly greater weight of the helium is, moreover, far more than offset by its chemical inertness, for as helium does not combine with oxygen it cannot explode or burn. Furthermore, its rate of diffusion is only about half that of hydrogen, and consequently it passes through the balloon fabric and wastes much more slowly. The chief advantage of helium, however, is obviously its incombustibility, for fire is one of the greatest of the hazards to which ordinary balloons are subject. Moreover, the use of a non-inflammable gas permits modifications in the design of airships which make for greater speed and cruising radius, as well as for greater military efficiency. In view of these advantages, it is apparent that the use of helium for inflating airships, both military and commercial, will be limited solely by the supply of helium available and the expense at which it can be produced.

The painstaking and little-noticed research which led to Prof. Cady's discovery of helium in natural gas, and the conception of another scientist ten years later that balloons might be made far safer and more efficient if inflated with helium, furnish an inspiring example of the practical value which purely scientific achievements may assume in course of time.—*Professional Paper* 121, U.S. Geological Survey, Department of the Interior.

## VENTILATION AND HUMAN EFFICIENCY.*

THE AUTHOR (Dr. Leonard Hill), in introducing his paper, said that Capt. S. R. Douglas and he had recently carried out some researches by making a spray of microbes into a room, where the windows were closed or opened; they had exposed culture plates after spraying a measured quantity of a dilute culture of an easily identified microbe which was carried up to the ceiling by means of a fan. Culture plates were exposed for two minutes in the different parts of the room after two minutes, and then after five minutes, and ten minutes, and so on, up to twenty minutes. The spray of microbes settled down by gravity, some of them on the plates. Then the plates were put into a warm chamber, and any microbe which had settled on the plate grew and multiplied into a colony. They had been able to distinguish the right microbe by the character of the colony. All those crowds of colonies were produced two minutes after making the spray in the room with windows open or closed.

A slide projected on the screen showed the difference in 20 minutes. Only one microbe had

*Discussion before the Institution of Mining and Metallurgy, October 27, 1921.

fallen on the plate with the window open, and the number that fell with the window shut could be seen. It was necessary to remember that all the people in a crowd who were speaking and sneezing and coughing were spraying out microbes from their throats and noses in a fine spray, just like the spray which had been used in the experiment. People who were carrying influenza and consumption and common colds, and so on, were throwing out those microbes and infecting other people in the room. If it were possible to get rid of those microbes a great deal would have been done towards improving health. They could not be got rid of altogether, but it was possible to lessen the massiveness of infection.

Mr. Greenwood gave him the clergy as the standard of health. The figures had been taken from the Registrar-General's reports A clergyman lived a regular life and did not indulge to excess like some weaker brethren might, but lived a life which was fairly easy and not very anxious. In some cases clergymen worked very hard, but on the whole they lived an easy life. They walked about and played games, and so on, and were a good deal in the open air. It would be seen that their death-rate at all ages was very low. It was a very good standard to take. The death rate of agricultural labourers with a low wage was a little higher. In spite of their low wage, by living an outdoor life and getting the garden produce, the green vegetables, and so on, which were very valuable to their health, they had the death-rate shown on the screen. Then they came to the cotton manufacturers who were higher, and shoe makers who were still higher, and the printers. Both from phthisis and from all causes the death-rate went up considerably with regard to the indoor factory occupations.

He had gone into the figures of the expectation of life of females with Mr. Greenwood. He had taken females because they were not so much damaged by other causes such as their occupation or trade. Females in Westmorland had at birth an expectation of life of 61 years, while in Middlesbrough at birth their expectation of life was only only 46 years. Such differences existed, if not quite so marked, on comparing all agricultural with city populations in England. The confined life of cities, whereby the population was crowded in tenements with warm moist stagnant air, compared to the open life on the hills, fields, and sea, was a great cause of sickness, loss of vigour, and enjoyment of life.

In proof of that they all knew that exposure naked to the sun and open air had a marvellous curative effect on slum children afflicted with tuberculosis and disease of the spine, and so on, as might be seen at Lord Mayor Treloar's Cripples' Hospital at Alton, under the care of Sir Henry Gauvain, or at Leysin in the Alps, under Dr. Rollier. He would like to show a few photographs just to illustrate how the children lived.

One slide shown on the screen showed the tubecular children naked, exposed to the open air and sun in the galleries. Their heads were carefully shaded, and the exposure of the body was gradual, otherwise the skin would blister. They got as brown as niggers, and their muscles got firm and hard, and their health improved, and their appetite went up. As had been proved lately at Treloar's Hospital by him and his colleagues, the heat production of the body was largely increased by that life in the open air, and that improved the appetite and all the other things, and effected the cure. Nothing was done except putting the limbs or back in splints and exposure to the open air and sun.

Another slide showed the children when they were better, when they could put off their splints, and do haymaking in the summer with nothing on but a loin cloth, and yet another showed the children skating in the Alpine winter with nothing on but a loin cloth. They lived that life, exposed to the sun and the cold air. There was a splendid cold air there which invigorated the muscles, and sent up the bodily heat production, and kept them vigorous, and the sun was keeping them warm and happy all the time by shining on their skin.

Children at Hayling Island from Treloar's Hospital went down to the sea and paddled and bathed every day whenever possible, and that increased the rapidity of cure very greatly indeed

He would come to the question of measuring the cooling and evaporative power of the air. Dr. Haldane had taken the wet-bulb as the measure, and pointed out that such-and-such a wet-bulb degree must be kept up. That was an exceedingly valuable criterion in confined places. J. L. Bruce in Australia preferred the dew-point rather than the wet-bulb. He (the author) had introduced an instrument called the katathermometer which took into account, not only the temperature, but the wind. The wind was the great thing which was cooling to the body. Too much wind was uncomfortable, but sufficient wind brought comfort.

The rate of cooling was measured between 100° and 95° F., and one took the mean for one's calculations as 36·5° C. (97·7° F.), and that was roughly skin temperature. The cooling power of the air per second was measured at skin temperature per sq. cm. of surface. The cooling power should not be translated straight away to the human body because the kata bulb was a very small thing, half the size of one's thumb, and in the large masses of the body, the limbs and the head and the trunk, the surface exposure compared to the mass was much smaller. The kata gave the cooling of a mouse rather than the cooling of the human body. One could empirically find out what were suitable cooling powers by taking measurements under all kinds of conditions where people were happy and comfortable, and those standards ought to be kept up in all mines, factories, and so on. By putting a muslin glove on to a katathermometer it was converted into a wet instrument and the cooling power by the wet katathermometer was then obtained. The dry one cooled by radiation and convection; the wet one cooled by radiation, convection, and evaporation; and the difference in the reading of the two gave the cooling by evaporation. The dry one represented the skin cool and dry, and the other one represented the skin sweating. The dry one was the more valuable in our factories and workshops, and the wet one was useful in climates, mines, &c., where there was a moist, hot atmosphere.

The cooling power had been studied in winds of different velocity in large wind tunnels at the National Physical Laboratory and at the East London College, and also by rotating the kata on a rotating arm. A diagram in the paper showed what cooling powers were obtained at different

temperatures with different winds. It would be seen that taking 20° C., to get a decent cooling power it would be necessary to have a wind getting on for one mile per hour. In order to get a cooling power of something like 6, which he considered a standard cooling power suitable for sedentary work, it would be necessary to have a wind of one mile per hour. Taking a temperature of 30° C., to get that cooling power it would be necessary to have a higher wind, and so on.

It would be seen what an enormous effect the wind had upon cooling power. That could be seen at once by taking some dry kata observations on different days. There were some given in his paper when the dry-bulb temperature was practically the same on different days, but the wind was very different. In one case it was a strong north wind; in another case it was a south-east wind of a moderate kind, and in another case it was almost calm. The dry kata reading was 56 in the first case, 27 in the second, and 13 in the third case. Clothing, of course, had a big effect upon the cooling powers. The details of the influence of clothing could be found in the second volume of his report on the Science of Ventilation and Open-Air Treatment, which was a special report to the Medical Research Council and could be obtained from His Majesty's Stationery Office

He had set up a standard of cooling power. The dry kata cooling power ought to be 6, and the wet kata cooling power ought to be 16 or 18—not less than that. He had found that those standards held good in rooms which appeared comfortable and fresh, where people were working quite happily and comfortably. Very often the figures which were obtained in factories were under those standards. A great number of observations had been taken by the Industrial Fatigue Research Board in different factories, and he had given some of those in the paper. For example, in potters' shops generally the dry kata readings were under the standard which he had given on cold days. With regard to warm days the readings were far under the standard which he had given.

A series of diagrams projected on the screen showed the same point. Those observations had been taken in printing shops in London during the previous winter and during the summer. The percentage of observations in different printing shops was given and the degrees Fahrenheit with the dry-bulb temperature.

One of the diagrams showed the wet-bulb temperature in the printing shops winter and summer. It would be seen that the wet-bulb temperature was beating up in the summer, but it was not very high, according to Dr. Haldane's standard. Occasionally it reached 72.

Another slide projected on the screen showed the dry kata and the wet kata. In the winter in printing shops a good many cases occurred where it was below his standard and some were above. He did not think that it mattered up to 8 because the men could work comfortably, but it was getting rather cold when it reached 9. In the summer it was found that readings were as low as 1 in some of the printing shops. Those were very bad conditions. With the wet kata his standard was 18, and in winter many readings were below that, and many more in summer.

The dry katathermometer could be used as an anemometer. They had worked out formulæ, and lately they had been able to thoroughly revise them; they had been able to work in the big wind tunnels, which they could not do during the war owing to the use of them for aeroplane work. They had had to modify their formulæ to some extent. They had never worked out the low velocities previously. It was hard to do that in wind tunnels, but they had done it on the rotating arm. In all that work he was very grateful to Miss Hargood-Ash, who was present that night showing the instruments. She had helped most patiently and excellently in all that work, and they had worked out the formulæ which they had given at the end of the paper. Air velocities could now be calculated quite accurately, he thought, with the katathermometer. In many factories they obtained air velocities which were very poor, even in winter, and poorer still in the summer.

Another slide projected on the screen gave frequency curves, worked out by the Industrial Fatigue Research Board in boot and shoe factories, of velocity as determined by the dry-bulb katathermometer in various methods of ventilation. It showed ventilation by open windows, and ventilation by roof cowls, and skylight windows in the winter and the summer. Then there was ventilation by various artificial methods. The extraction by fan came out the best, giving the highest velocities, and the plenum came out the worst.

Another slide showed the combined plenum and extraction system, such as one might introduce with a fine current sweeping through the mine or factory, so as to keep the evaporative power sufficient to sweep away the dust and sweep away the microbes exhaled by the people. That seemed to be the most ideal artificial form of ventilation.

In South African mines Dr. Orenstein and Mr. Ireland had been using the katathermometer for estimating the effect of atmospheric conditions on output and fatigue, and the diagram showed that output was lowest when the dry kata cooling power was lowest.

Further evidence concerning efficiency was given in his paper.

[Slides were then shown illustrating the electrical katathermometer and the recording electrical katathermometer. These instruments were demonstrated by Miss Hargood-Ash after the meeting.]

Dr. J. S. Haldane said that Dr. Hill had brought forward the subject of ventilation in such a clear and full manner that at first sight it might seem that there was nothing left for him to add. There were a few points, however, on which they did not altogether agree, or on which, at any rate, he thought there was room for discussion. On the whole, however, he was in cordial agreement with a great part of what Dr. Hill had so admirably said.

Dr. Hill had referred to an old report of a Departmental Committee of which he (Dr. Haldane) had been Chairman, on the subject of the standard of carbonic acid in factories, and he had pointed out that the comfort of a room did not depend on the carbonic acid. That was a fact with which he cordially agreed. In fact, he could add volumes to the evidence which Dr.

Hill had given on that subject. Perhaps the evidence from submarines was the most clear. During the war a submarine was often submerged for 20 hours at a time, and for various reasons could not show its nose above water. The air under those conditions got pretty bad chemically; in fact, after a few hours no light would burn in the air, but it was quite comfortable so long as the carbonic acid did not go higher than about 3 per cent. If the carbonic acid went higher, people at' rest in the submarine were still quite comfortable, though breathing a good deal deeper than usual; but men working the planes could not do so properly because they were panting. Therefore, it was necessary to keep down the percentage of carbonic acid in the air.

But the air from a chemical point of view was atrocious. If a match was struck it just fizzled and that was all, and a light went out as if you were putting it into water. No one was aware of anything unusual in the air until they saw the effect on a light. An officer entering the submarine as she was opened up told him that the air was like that of a high mountain; he noticed the increase in breathing, but smelt no bad smell and felt nothing unpleasant, and he thought the air was quite good—and so it was with a clean and healthy crew on board. The whole secret was, as Dr. Hill had pointed out, that the place was cool. The sea water kept the submarine perfectly cool, and condensed any excess of moisture there might be on the walls. One could sleep there quite soundly. He had slept there as soundly as he had slept at home.

That was only one more example pointing the moral of what Dr. Hill had said. But coming back to that standard of ventilation, he was not going to agree that that standard, taken in conjunction with the recommendations as to temperature, was not a useful one. A standard of 12 parts per 10,000 of carbonic acid in the air represented a certain moderate degree of freedom from the germs which Dr. Hill laid such stress on in a further paragraph. That standard only represented what was practicable at the time. It was the result of a great many observations in factories in different parts of the country. They were not thinking of whether the air was warm or cool, but of the exchange of air necessary for the purpose of keeping down infection as far as possible. They would have liked to have said that the standard should be a much higher one, but that did not seem attainable. He had served on a committee in the Navy just before the war where they had gone in for a far higher standard because there was no end of power available for ventilation purposes on battleships.

He agreed with nearly all that Dr. Hill had said on the subject of dust, but he thought that there was one point on which perhaps they did not quite agree, and that was as regards the final effect of what Dr. Hill called a harmless dust. He (Dr. Haldane) would call a harmless kind of dust the sort of dust which was present in smoke particles or coal dust, or the shale dust which was inhaled by coalminers to such a large extent. He did not think that habitual inhalation of a moderate amount of that dust did any harm in the long run. At any rate, it appeared to him that the evidence that it did harm and produced a state of chronic asthma or bronchitis was not reliable. He had discussed that matter in a paper several years previously before the Institution of Mining Engineers, and he had analysed the records of the death-rates for different occupations and come to the conclusion that there was no evidence that the dust ordinarily breathed in a coal mine did any harm in the end to the coal miners. He would say the same for the smoke in towns. He did not believe that the smoke in towns injured people's lungs, or at any rate, he did not believe it accumulated in them. People had in their lungs an astoundingly efficient service of phagocytes whose business was to remove solid particles, including bacteria. If that service was given plenty to do it probably became more efficient, and this was perhaps one of the reasons why coalminers, though they were exposed to much dust, had extraordinarily little phthisis Moreover, they breated not only coal dust, but a large quantity of shale dust containing a third or more of quartz. Probably a coalminer breathed much more quartz than a goldminer. The harmlessness of quartz in a coal mine seemed to depend on its admixture with coal dust, &c., which stimulated the phagocytes to do their work, whereas a perfectly inert dust like quartz unmixed with substances like coaldust did not.

At some places they found miners breathing enormous quantities of silica and quartz with no harm at all. It was mixed with something else which somehow or other led to its being excreted by the lungs so that they did not suffer. It would be seen from that why he did not take much interest in general standards of how many particles of dust should be in the air. It all depended on the kind of dust and the size of the particles. Some kinds of dust were so deadly if they were breathed for long periods, that it was extraordinarily important to keep the air as free from the dust as possible, or else to mix the dust with something which would render it harmless.

Dr. Hill had laid great stress on bad effects from a low cooling power in air. He (Dr. Haldane) frankly said that he did not, provided that men could still regulate their body-temperatures. He believed that a mine, however warm it was up to a certain point, and however moist it was up to a certain point, ought to be a perfectly healthy place, and was so, except where there were other causes of unhealthiness. Dr. Hill had referred to the Cornish miners who suffered very much from miners' phthisis. This was certainly due to the dust, but as to any bad effects of the heat, he really did not think there were any. In the first place, the great majority of them worked in fairly cool places and they suffered from phthisis just the same, and had the same death-rate. In the second place, they found men working coal mines all over the country, under, in many cases, even more trying average conditions of heat than in Cornish mines. There were some fearfully hot places in the Cornish mines certainly, but they were very exceptional.

He did not think it mattered at all as regards heat, whether the men went to cinema shows afterwards. What mattered was what infection

they got there. He thought that a man who was accustomed to heat, and was accustomed to regulating his temperature during hard work, would stand an atmosphere a good deal more warm than a person who was not. If a person were engaged in literary work or something that did not make him sweat, and he was put down into a mine or a fairly warm place, he would get faint or get a bad headache, or even a violent attack of diarrhoea; but if he got accustomed to the warm air he was all right. The same thing applied to miners. If they put a man who was not accustomed to heat into a hot mine it would bowl him over, and he would have to come out. He had to get acclimatised. So far as his observations had gone he did not think it mattered to a man's health whether the air had less cooling power relatively to other places, so long as he could keep his body temperature from going up.

If it were not so, where would they all be if they went to a tropical country, or went to Australia even. With regard to the conditions there during a great deal of the year as measured by the katathermometer, there would be much less cooling power than there was in England, but the people in Australia were very well and vigorous, and they were very well in most tropical countries if they could avoid infection and tropical diseases, and they could work vigorously provided the cooling power of the air was sufficient to enable the body to regulate its temperature during work.

He did not think that the high expectation of life in Westmorland had anything to do with cooling power. He did not see any evidence of it. There were other causes at work. Babies, for instance, in Westmorland, were properly looked after by their mothers in Nature's way. In Middlesbrough they found a very different state, and there was a tremendous death-rate amongst infants, which was now fortunately being tackled all round. A sweeping reduction had been brought about in the last few years in the infantile death-rate. That, at once, put up the expectation of life in a place like Middlesbrough; and all the other conditions could be taken one by one, he thought He could not believe that it had much to do with the cooling power of the air. He also thought that the existing evidence showed clearly that the pneumonia among natives brought to the Johannesburg mines was not due to underground conditions. It had been dealt with successfully on a quite different theory.

He would like to say something about the significance of the wet-bulb temperature. First of all with regard to taking the dew-point as a guide. Dr. Hill had mentioned that an Australian investigator regarded the dew-point as a better guide than the wet-bulb, and had fixed 62 as the permissible maximum dew-point. If that was the permissible maximum all he could say was that that permissible maximum was very constantly being exceeded, and they could not help its being exceeded. But if anyone said that the dew-point could be taken as a guide he would be inclined to pay as much attention to him as if he argued that the earth was flat. This was because such an idea was entirely contrary to evidence of the most definite kind and to the whole physics of the subject. He did not want anyone to go away thinking there was any doubt on this subject; there was none.

Then with regard to the katathermometer. That was an instrument which, as Dr. Hill had so clearly explained, told one the cooling power of the air; and he thought it was an admirable scientific instrument for that purpose. It took into account the movement of the air, the wet-bulb temperature, the dry-bulb temperature, and everything else all in one sweep. Dr. Hill had said that he (Dr. Haldane) was rather inclined to take the wet-bulb as a more useful guide. So he was, on the whole He thought the reason would be evident to anyone who had to do practically with looking after the temperature and the working conditions in mines. The reason was that taking, for instance, a working face in a coal mine, some of the men were in a good air current, some were holing the coal under the seam and were out of the air current, and the air current varied very much in different parts. If the reading of the katathermometer were taken in the air current they would get one reading, and if it were taken underneath the coal where the men were holing, they would get another reading.

He thought that the wet-bulb temperature gave them on the whole a more useful indication of the conditions. In any case it was necessary in order to be able to control the conditions to find out what was wrong when the katathermometer indicated that something was wrong. It was necessary to know what the dry-bulb temperature was and particularly what the wet-bulb temperature was. That was the only reason why he was inclined to lay very great stress on wet-bulb readings, although the katathermometer gave everything together and gave the whole effect There was one thing he desired to say with regard to both wet-bulb temperature and katathermometer readings. They seemed to him to be of little direct significance in mines until they were getting near the point at which the body was unable to regulate temperature any further.

If men were put to work where the wet-bulb was too high or the wet-bulb *plus* the air current were not satisfactory, the only thing that happened was that they would not work Miners knew quite well what they were doing. The only instances in which he knew of direct harm to them through heat were cases where men had gone on working through some urgent necessity in temperatures in which they would not work ordinarily; for instance, in rescue work. In the case of saving life they would risk their lives, but they would not risk their lives for the purpose of getting mineral. It was necessary to see that the conditions were such that the men could do full and efficient work, and unless they were pushing physiological means of regulation too hard there was not much difficulty.

The Committee of the Institution of Mining Engineers had come to that conclusion as regards mines in England: that there was no difficulty with proper ventilation in keeping the conditions such as would enable them with proper ventilation to go far deeper in coal mines than at present. In the Transvaal it was very much easier because of the very much lower geothermic gradient than in this country. The ventilation could be regulated so that a man's body temperature did not go up, and he submitted that as long as that was so the man's life ought to be perfectly healthy—and he believed it was. At any rate he would

like to have more evidence than had been brought before them to show the contrary.

Mr. ROBERT MCLAREN, M P., said that as a visitor he would like to say that it had given him very great pleasure indeed to listen to Dr. Hill's paper. With a great deal that had been said he was in entire agreement, but what he noticed in connection with all scientific societies was that sometimes they forgot the practical side. The instrument on the table which had been shown upon the screen was an excellent instrument, but the difficulty that he had was that hundreds of them would be required in some of the large mines to indicate exactly the conditions of the mines as far as ventilation was concerned. He was also reminded when he saw that instrument of one which he had invented himself which was going to do great things, but when they took it down the mine they found that it was not only costly, but that it did not come up to what they had expected. For that reason he had very little faith in instruments used underground ever since.

Dr. Haldane had spoken very clearly on the question of the ventilation of those mines which concerned him (Mr. McLaren) most of all. He could, from the practical side, corroborate what Dr. Haldane had said with regard to the miners who swallowed a good deal of coal dust. Many years previously when he was a younger man it used to be said about men living in his district, which was a mining district entirely, that they died very soon through asthma of phthisis because of the swallowing of coal dust. When Dr. Haldane gave it forth to the world that coal dust after all did not affect the miners' lungs, but was sometimes a help to the miners, it was no surprise to him to learn it, because in those days the reason why the miners suffered from phthisis was because of the carbonic acid gas given off in the mines and the want of ventilation In the same district under existing conditions they found men working in the mines who were over 60 years of age, strong and healthy, and evidently the mines agreed with them. Those men, he knew for a fact, swallowed a good deal of coal dust. It was perfectly evident then that the question of ventilation was the first thing that ought to concern he mining management of any colliery. Personally, when he used to be a Government Inspector of Mines, he forgave a colliery manager a great deal if he found he provided a good ventilation.

It was perfectly evident to anybody who knew anything about the management of mines that there must be different temperatures throughout the mine. If one took the case of a large mine which extended perhaps for miles, it was apparent that that part of the mine which got fresh air to begin with was relatively fresh and pure and cool, but when one went further in the air became contaminated for various reasons over which no one had any control. There were the gases given off by the coal, and the gases generated by the breathing of the men themselves, and from their lamps.

(To be continued.)

# CORRESPONDENCE.

## PHARMACY ACTS AMENDMENT BILL.

*To the Editor of the Chemical News.*

SIR,—I am instructed by the Council of the Institute of Chemistry of Great Britain and Ireland to direct your attention to the following letter which has been addressed to Capt. James O'Grady, J.P., M.P., Col. D. Watts Morgan, D.S.O , M P., and Mr. Thomas W. Casey, M.P.—I am, &c

RICHARD B. PILCHER,
*Registrar and Secretary.*

*November 17, 1921.*

PHARMACY ACTS AMENDMENT BILL.

SIR,—The attention of the Council of the Institute of Chemistry of Great Britain and Ireland has been directed to "a Bill to regularise the position of all persons trading as chemists and druggists or pharmacy store proprietors in the sale of drugs, the dispensing of doctors' prescriptions, and the sale of medicine."

The official print states that the Bill was presented by Captain O'Grady, and supported by Col. Watts Morgan and Mr. Casey.

In this Bill reference is made to "the Incorporated Society of the Institute of Chemistry" and to "the Institute of Chemistry."

The Institute of Chemisry of Great Britain and Ireland is the only body in this country incorporated by Royal Charter whose title contains the words "Institute of Chemistry," and the Council of the Institute desire me to inform you that they have not been consulted with regard to the provisions of this Bill and have not had any information regarding its promotion.

The Institute of Chemistry is established to examine and register persons found competent to practise chemistry in its applications to the arts and manufactures, as distinct from those who practise pharmacy and are engaged in the sale of drugs and medicines, and in the dispensing of prescriptions.

The Council of the Institute deplore the confusion which arises through the application of the term "chemist" to two distinct callings, and they would welcome any legislation which would tend to remove this confusion.

They hold that the use of the distinctive titles "chemist" and "pharmacist" to denote these callings would tend to the general recognition of the difference between them and to the removal of a confusion which exists in no other country.

The Council wish to dissociate themselves from the suggestion that they should be represented on the Central Council, which it is proposed in the Bill shall be concerned with the Pharmaceutical Register, and from taking any part in the examination and registration functions vested by Royal Charter and the Pharmacy Acts in the Pharmaceutical Society of Great Britain. The Council do not feel called upon at present to comment upon the other provisions of the Bill.—I am, &c.,

(*Signed*) RICHARD B. PILCHER,
*Registrar and Secretary.*

## NOTES.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 5th inst., Sir James Crichton Browne, Treasurer and Vice-President in the Chair. Mr. A. K. Loyd was elected a Manager to fill the vacancy caused by the death of Mr. J. H. Balfour Browne; Dr. Niels Bohr (Copenhagen), Dr. Johan Hjort (Copenhagen), and Prof. Paul Langevin (Paris) were elected Honorary Members; and Mr. W. A. F. Balfour Browne, the Dowager Countess of Carnarvon, Mr. P. C. Clifford, Mr. and Mrs. C. L. Dalziel, Major F. R. de Bertodano, Lieut.-Col. F. J. Dewes, Mr. H. J. Eck, Mr. K. Lightfoot, Mr. W. M. Ogilvie, Mr. R B. Ransford, and Mr. F. I. Rawlins were elected Members.

We understand that the State Electricity Commission of Australia has given to a Wolverhampton firm what is possibly the largest order undertaken in this country. The summary of the contract is as below, and it has been secured in spite of severe American competition, and certainly indicates a revival of trade. "Twelve 'Thompson' Patent Straight Vertical Water-Tube Boilers, working pressure 260lb. per sq. inch each to evaporate 70,000lb of steam per hour, fitted with superheaters to superheat the steam to a final temperature of 650° F. Each boiler will be fitted with three Underfeed Forced Draught Travelling Crate Stokers to burn Morwell Brown Coal. This coal, we believe, is found practically on the earth's surface, and the Power Station is being erected adjacent into the fuel bed, and is for the purpose of supplying power to Morwell and district. The boilers will be complete with chimneys, flues, and automatic soot and ash extracting and disposal plant."

Board of Trade Announcement.—The Board of Trade give notice that in exercise of the powers conferred upon them by Part II. of the Safeguarding of Industries' Act, 1921, they have referred to a Committee constituted for the purposes of that part of the Act and consisting of: Sir William Ashley, Ph.D. (Chairman); Mr. J. Arthur Aiton, C.B.E.; Sir Thomas W. Allen; Sir John N. Barran, Bt.; and Mr. F. R. Davenport; a complaint by the British Flint Glass Manufacturers' Association and the National Flint Glass-Makers' Society, that articles of domestic glassware, illuminating glassware, and mounting glassware, manufactured in Germany and Czecho-Slovakia, are being sold or offered for sale in the United Kingdom at prices which by reason of depreciation in the value in relation to sterling of the currency of the above-named foreign countries are below the prices at which similar goods can be profitably manufactured in the United Kingdom, and that by reason thereof employment in the glass industry in the United Kingdom is being or is likely to be seriously affected. The Commitee are directed after ascertaining the facts to report to the President of the Board of Trade (*a*) whether the conditions specified in Section 2, Sub-Section (1) of the Safeguarding of Industries Act, 1921, are fulfilled; (*b*) on the effect which the imposition of a duty under Part II. of the Act on goods of the class or description covered by the complaint would exert on employment in any other industry being an industry using goods of that class or description as material; and (*c*) whether in the opinion of the Committee production in the industry manufacturing similar goods in the United Kingdom is being carried on with reasonable efficiency and economy. The Committee propose to hold their first sitting for the taking of evidence at 2.30 p.m. on Monday, December 12, 1921, at the Hotel Windsor, Victoria Street, London, S.W.1 The Secretary to the Committee is Mr. W. G. Fergusson, Board of Trade, Great George Street, London, S.W.1, to whom all communications should be addressed.

We have received from the Secretary and Editor of the Faraday Society a copy of the "Report of a General Discussion on Electro-depositions and Electro-plating" that resulted from a joint meeting of the Faraday Society and the Sheffield Section of the Institute of Metals, on Friday, November 19, that was in the Sheffield University. The Report, which is well printed and illustrated, will form a very valuable reference book on the technicalities of electro-deposition; the papers are of exceptional interest, and deal exhaustively with the subject and include electroplating as prevention of corrosion, deposition of cobalt, gold-silver alloys, the use of colloids in the electro-deposition of metals, crystalline structure of electro-deposited silver, and many kindred matters, together with discussions by those present at the meeting. We have already drawn attention to the valuable work that is being done by the Faraday Society in arranging and publishing these important discussions, and we append a list of the papers that can be obtained by application to the Secretary, 10, Essex Street, W.C.2, and prices. The Microscope: Its Design, Construction and Applications (bound in cloth), 21s. The Present Position of the Theory of Ionisation, 12s. 6d. Occlusion of Gases by Metals, 5s. The Co-ordination of Scientific Publication, 3s. Electric Furnaces, 3s. 6d. The Setting of Cements and Plasters, 5s. 6d. The Training and Work of the Chemical Engineer, 3s. 6d. The Attainment of High Temperatures in the Laboratory, 2s. 6d. The Transformations of Pure Iron, 2s. 6d. The Passivity of Metals, 3s. 6d. The Constitution of Water, 2s.

Queensland Mineral Pigments.—Mr. Joseph Campbell, an Australian scientist, has devoted three months to a special study of the triassic rocks lying to the north of Cooktown, Queensland. These rocks yield, among other things, valuable oxides and ochres, and at Cape Flattery in particular there is scope for a large industry in pigments. Last year Australia imported 1,636 tons of dry colours of all tints, valued at £85,990. Cape Flattery alone can produce a large proportion of such pigments at a much lower cost than that at which they are imported. A sample of red oxide (Indian red) from this source was found by the Government Analyst of Queensland to contain the following percentages: Loss on ignition (*i.e.*, moisture, 7·3; silica and insoluble, 23·2; oxide of iron, 61·4; alumina, 8·0; total, 99·9. It is interesting to compare this with the following analysis of an ordinary Indian red: ferric oxide, 43·82; alumina, 28·30; silica, 23·16; calcium carbonate, 3·15; loss on ignition (water) 1·45; total, 99·88 per cent. If calcium carbonate is required in the Cape Flattery red, it is easy to supply it from the coral reef around, which can be pulverised for the purpose.

# New Patents.

THIS List is specially compiled for the *Chemical News* by Messrs. Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W.C.2, from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

30124—Commin, F H.—Process for fixation of atmospheric nitrogen November 11

30471—Barrett, Co.—Process for purification of hydrocarbons. November 15

30520—Morris, E. F.—Electrolysis of acetone solutions. November 16

30612—Imray, O. Y.—Manufacture of derivatives of dihydro-isoquinoline. November 16

30691—Rigby, T.—Utilization of industrial waste products November 17

*Specification published this Week.*

142806—Barrett, Co —Manufacture of resin from naphthas

170880—Matheson, E.—Manufacture of sulphuric acid

146407—Berger, H.—Manufacture of an improved nickel catalyst

170991—Wolffenstein, R.—Production of solutions containing aluminium formate and an alkali-salt

170964—Bronnert, E —Process for production of high-percentage sulphite cellulose

*Abstract Published this Week*

*Sulphur-terpene Compounds.*—Patent No 169513.—Terpenes, or certain derivatives such as terpineol, or rosin are heated with sulphur to produce brittle solids, or semi-solids according to the duration of the heating, sulphuretted hydrogen is evolved. In an example, equal parts of oil of turpentine and sulphur are heated together for three hours at a temperature rising from 150-200°.C., yielding a neutral brittle mass soluble in turpentine, toluene, and xylene; the quality of gas evolved may serve as a check on the progress of the reaction. The products from non-colloidal solutions and may be used, either alone or in toluene, xylene, etc solution with or without addition of rubber, for coating or impregnating materials, they may also be vulcanized on to or with rubber and can be moulded. If a semi-solid product is employed, further heating effects conversion to the harder products; for example, if mixed with wood pulp and heated in a press, a hard solid mass results.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

## MEETINGS FOR THE WEEK

*Monday, December 12.*

Royal Society of Arts, 8 "Processes of Engraving and Etching," by Arthur M. Hind

*Tuesday, December 13*

Chemical Society, 7.45 (Annual General Meeting). "Structure of some Gaseous Molecules, by Prof A. O. Rankine

*Wednesday, December 14.*

Royal Society of Arts, 8 "Trade with the Netherlands, East Indies," by Sir Walter B. Townley

*Thursday, December 15.*

Chemical Society, 8. "Researches on Residual Affinity and Co-ordination," by G. T. Morgan and J. D Main Smith

Institution of Electrical Engineers, 6. "Induction-Type Synchronous Motors," by L. H. A. Carr



## NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemica Apparatus, &c., for review or notice to be addressed to the EDITOR.

**SUBSCRIPTIONS,** £1 12s. per annum, payable in advance should be addressed to the MANAGER.

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THE CHEMICAL NEWS.

VOL. CXXIII., No. 3218.

## INDUCED REACTIONS AND NEGATIVE CATALYSIS.*

By N. R. DHAR and N. N. MITTRA

IF A and B chemically react with one another, while A and C do not under ordinary conditions, but do so in the presence of the former reaction, the second reaction is said to be induced by the first; in other words, a chemical change between one set of substances is capable of forcing or inducing a chemical change between another set of substances having the potentiality to undergo a chemical change. For instance, when an acqueous solution of mercuric chloride is boiled with oxalic acid, there is no reduction of the mercuric chloride to the mercurous state, but as is well known this mixture of mercuric chloride and oxalic acid decomposes at the ordinary temperature in sunlight according to the equation:—

$$2HgCl_2+H_2C_2O_4=2HgCl+2HCl+2CO_2.$$

The same change, however, takes place in the dark (Dhar, *Jour. Chem. Soc.*, 1917, cxi., 690) if a few drops of a decinormal potassium permanganate are added to the mixture; as soon as the colour of the permanganate is discharged mercurous chloride begins to separate out.

This phenomenon appears to be of general occurrence. Thus it has been found out that the reduction of mercuric chloride and bromide by oxalic acid, tartaric acid, citric acid, malic acid, malonic acid, glycollic acid, cane sugar, grape sugar, glycerine, lactic acid, hydroxylamine hydrochloride, hydrazine hydrochloride, &c., the reduction of gold chloride by several reducing agents, and the reduction of silver nitrate, cupric chloride and selenious acid (to selenium) by various organic acids are promoted by the addition of such oxidising agents as potassium permanganate, potassium persulphate, manganese dioxide, potassium nitrite, hydrogen peroxide, ceric salts, &c. (Dhar, *Proc. Akad. Vetensk, Amsterdam*, 1921, xxiii., 1074).

It is a remarkable fact that this effect is particularly noticeable in those reactions, which are very sensitive to light.

To investigate further the general occurrence of induced reactions, the following cases have been studied.

According to the customary nomenclature, the faster reaction is called the primary reaction and that which appears to be forced along or induced by contact with the primary change is called the secondary reaction. The substance which takes part in both reactions is called the actor, the substance which takes part in the primary reaction is called the inductor, and the substance which takes part in the secondary reaction is called the acceptor. The way in which the inductor acts is not known, and hence these induced reactions form a branch of catalysis (see Table I.).

In all the above-mentioned cases at first the primary change, that is, the oxidation of the easily oxidisable substance takes place and this primary change induces or promotes the secondary or the induced change, that is the oxidation of the difficultly oxidisable substance.

In several of these induced reactions we determined the induction factors, but unfortunately hardly any conclusion could be drawn from these induction factors as to the mechanism of these changes.

It is well known that a solution of sodium arsenite is not oxidised by atmospheric oxygen under ordinary conditions. On the other hand, a solution of sodium sulphite is readily oxidised to sodium sulphate.— Now if we mix the two together, both the oxidations go on simultaneously. At the same time a curious phenomenon takes place. The velocity of the oxidation of sodium sulphite becomes very small in presence of sodium arsenite, that is, sodium arsenite which is undergoing a slow oxidation acts as a powerful negative catalyst in the oxidation of sodium sulphite. Similarly a solution of oxalate which also undergoes slow oxidation in presence of sodium sulphite, which is itself being oxidised, slows down to a marked extent the oxidation of sodium sulphite by atmospheric oxygen. Moreover, we have observed that manganous hydroxide, ferrous hydroxide, and sodium thiosulphate which are slowly oxidised by passing oxygen in presence of a solution of sodium sulphite markedly retard the oxidation of sodium sulphite. Also ferrous salts retard the oxidation of stannous salts in air. It appears probable, therefore, that the phenomenon of negative catalysis is possible only when the catalyst is liable to be oxidised. These cases are of great importance in connection with the controversial question of negative catalysis.

In a previous paper (Dhar, *Jour. Chem. Soc.*, 1917, cxi., 707) it has been shown that manganous salts act as powerful negative catalysts in the oxidations of formic and phosphorous acids by chromic acid, and manganous salts can easily pass into the manganic state Moreover, it has been shown by various investigators that some organic substances notably quinol, brucine, &c., act as negative catalysts in the oxidation of sodium sulphite by oxygen, and all these organic substances are themselves readily oxidised. It is well known that the oxidation of phosphorus by oxygen of the air is retarded by the vapours of various organic substances, *e.g.*, ether, alcohol, turpentine, &c., and the oxidation of chloroform is retarded by the presence of a small quantity of alcohol. Now all these negative catalysts are good reducing agents, and are themselves readily oxidised. Hence in oxidation reactions the phenomenon of negative catalysis takes place when the catalyst itself is liable to be readily oxidised.

If we expose a mixture of sodium sulphite and sodium arsenite to atmospheric oxygen, according to Schönbein (*Jour. Prakt. Chem.*, 1858, lxxv, 99) one atom of oxygen should go to oxidise sodium sulphite, while the other atom would oxidise a molecule of sodium arsenite in the same time. The oxidation of sodium arsenite is a very slow chemical change and in order that Schönbein's law be applicable, it follows immediately that the oxidation of sodium sulphite which is fairly rapid, should become a slow change, and the velocity of this oxidation should become equal to that of the

* Read before The Faraday Society, November 28, 1921

TABLE I.

| Primary change | Secondary change | Actor | Inductor | Acceptor |
|---|---|---|---|---|
| $HgCl_2+Na_2SO_3$ | $\rightarrow HgCl_2+Na_3AsO_3$ | $HgCl_2$ | $Na_2SO_3$ | $Na_3AsO_3$ |
| $HgCl_2+H.COOH$ | $\rightarrow HgCl_2+Na_3AsO_3$ | $HgCl_2$ | $H.COOH$ | $Na_3AsO_3$ |
| $HgCl_2+Na_3PO_3$ | $\rightarrow HgCl_2+Na_3AsO_3$ | $HgCl_2$ | $Na_3PO_3$ | $Na_3AsO_3$ |
| $HgCl_2+Na_2SO_3$ | $\rightarrow HgCl_2+H_3AsO_3$ | $HgCl_2$ | $Na_2SO_3$ | $H_3AsO_3$ |
| $HgCl_2+Na_3PO_3$ | $\rightarrow HgCl_2+H_3AsO_3$ | $HgCl_2$ | $Na_3PO_3$ | $H_3AsO_3$ |
| $Na_2SO_3$+air | $\rightarrow NaNO_2$+air | air | $Na_2SO_3$ | $NaNO_2$ |
| $Na_2SO_3$+air | $\rightarrow K_2C_2O_4$+air | air | $Na_2SO_3$ | $K_2C_2O_4$ |
| $Na_2SO_3$+air | $\rightarrow Fe(NH_4)_2(SO_4)_2$+air | air | $Na_2SO_3$ | $Fe(NH_4)_2(SO_4)_2$ |
| $Na_2SO_3+O_2$ | $\rightarrow Fe(OH)_2+O_2$ | $O_2$ | $Na_2SO_3$ | $Fe(OH)_2$ |
| $Na_2SO_3+O_2$ | $\rightarrow Co(OH)_2+O_2$ | $O_2$ | $Na_2SO_3$ | $Co(OH)_2$ |
| $Na_2SO_3+O_2$ | $\rightarrow Ni(OH)_2+O_2$ | $O_2$ | $Na_2SO_3$ | $Ni(OH)_2$ |
| $Na_2SO_3+O_2$ | $\rightarrow Cu_2+O_2$ | $O_2$ | $Na_2SO_3$ | $Cu_2O$ |
| $H_2SO_3$+air | $\rightarrow FeSO_4$+air | air | $H_2SO_3$ | $FeSO_4$ |
| $H_2SO_3$+air | $\rightarrow SnCl_2$+air | air | $H_2SO_3$ | $SnCl_2$ |
| $Fe(OH)_2+O_2$ | $\rightarrow Ni(OH)_2+O_2$ | $O_2$ | $Fe(OH)_2$ | $Ni(OH)_2$ |
| $Co(OH)_2+O_2$ | $\rightarrow Ni(OH)_2+O_2$ | $O_2$ | $Co(OH)_2$ | $Ni(OH)_2$ |
| $Mn(OH)_2+O_2$ | $\rightarrow Ni(OH)_2+O_2$ | $O_2$ | $Mn(OH)_2$ | $Ni(OH)_2$ |
| $Ce(OH)_3+O_2$ | $\rightarrow Ni(OH)_2+O_2$ | $O_2$ | $Ce(OH)_3$ | $Ni(OH)_2$ |
| $Na_2SO_3$+air | $\rightarrow Na_3AsO_3$+air | air | $Na_2SO_3$ | $Na_3AsO_3$ |
| $Na_2SO_3$+air | $\rightarrow Mn(OH)_2$+air | air | $Na_2SO_3$ | $Mn(OH)_2$ |
| $Na_2SO_3$+air | $\rightarrow Na_2S_2O_3$+air | air | $Na_2SO_3$ | $Na_2S_2O_3$ |
| $SnCl_2$+air | $\rightarrow Fe(NH_4)_2(SO_4)_2$+air | air | $SnCl_2$ | $Fe(NH_4)_2(SO_4)_2$ |

oxidation of sodium arsenite, because the same amount of oxygen will be taken up by the reducing agents in the same time. As a matter of fact, from our experiments we have observed that in the presence of sodium arsenite, or potassium oxalate, or manganous hydroxide or ferrous hydroxide, the velocity of the oxidation of sodium sulphite by air becomes very small. We assume that a molecule of oxygen splits up in this reaction into two atoms and each atom oxidises one of the reducing agents. Now as a solution of sodium sulphite is much more readily oxidised than a solution of sodium arsenite, it becomes difficult to understand why the other oxygen atom, instead of attacking the readily oxidisable unacted sodium sulphite, attacks the much more difficultly oxidisable sodium arsenite. Or if we assume that at first a peroxide of the type of Bodländer's benzoyl peroxide (Ahren's *Sarum*, 1899, iii., 470) is formed as a combination of the sodium sulphite with a molecule of oxygen, we are still encountered with the same difficulty. In this case we will have to assume that this peroxide instead of attacking the readily oxidisable unattacked sodium sulphite will attack the less readily oxidisable sodium arsenite by preference. It seems therefore, that the only course left to us is to find out the explanation in the view of the formation of a complex of sulphite and arsenite, or of sulphite and oxalate, and that this complex is oxidised as a whole. It is well known that complex oxalates and sulphites do exist.

It has been observed in a previous paper (Dhar, *Proc. Akad. Vetensk.*, Amsterdam, 1920, xxiii., 299) that in the oxidation of sulphites and sulphurous acid, the sulphite ion is the active agent. On the addition of an arsenite to a sulphite, a complex, which it self is oxidised as a whole, is formed. At the same time the velocity of the oxidation of the sulphite becomes less due to the decrease in the concentration of the sulphite ions arising out of the formation of a complex of sulphite and arsenite or oxalate. Hence it seems that the only plausible explanation of the negative catalysis stands on the hypothesis of the formation of an intermediate complex compound.

Now there is no chemical change between potassium oxalate and mercuric chloride in the dark at the ordinary temperature, though the following chemical change takes place in light,

$$k_2C_2O_4+HgCl_2=2HgCl+2kCl+2CO_2.$$

If to this mixture of oxalate and mercuric chloride we add a ferrous salt, one gets a slight precipitate of ferrous oxalate, and at the same time mercurous chloride is formed. A solution of ferrous salt cannot reduce mercuric chloride at the ordinary temperature, but in presence of an oxalate it becomes a better reducing agent and reduces mercuric chloride to the mercurous state, and at the same time the potential reducing power of an oxalate is activated in bringing forth the reduction of mercuric chloride to the mercurous state. Evidently the reducing power of the ferrous salt as also that of the oxalate is activated by their mutual presence. Tartrates and citrates behave in a similar manner in presence of ferrous salts. Ferrous and ferric salts accelerate the formation of mercurous chloride from an oxalate and mercuric chloride solution when exposed to light. Winther (*Zeit. Wiss. Photo Chem.*, 1909, vii., 409) has brought forward argument to show that the light sensitiveness of a mixture of an oxalate and mercuric chloride is due to the presence of iron, and this investigator suggests that the purest mixtures of an oxalate and mercuric chloride so far prepared have contained iron. In absence of iron the mixture is not sensitive to visible rays. It seems to us that the real function of iron, if it is present, is that of a photoferment or photo catalyst as suggested by Winther, as well as that of an inductor. The ferrous salt in presence of an oxalate reduces the mercuric chloride to mercurous state, and at the same time activates the potential reducing power of the oxalate in indcing the reduction of mercuric chloride to the mercurous state. This induced reaction takes place also in the dark.

On investigating these various cases of induced reactions we were naturally led to the more general conclusion that one chemical change should induce another chemical change of the *same type*, and we tried to verify this conclusion.

We found that the reduction of mercuric chloride by such different reducing agents as formic acid, sulphurous acid, phosphorous acid, &c., induce in all cases the reduction of the same substance, *e.g.*, mercuric chloride, by sodium arsenite. We also investigated other changes, as for instance, the decomposition of unstable substances. It is well known that ammonium dichromate decomposes readily into nitrogen, water and chromium oxide, also the decomposition temperature of potassium persulphate is lower than that of potassium chlorate, and it has been found that in presence of decomposing ammonium dichromate or persulphate the decomposition temperature of potassium chlorate is appreciably lowered. In this connection it will be of interest to investigate whether the presence of an easily decomposable explosive will lower down the decomposition temperature of a difficultly decomposable explosive, and this investigation will throw light on the velocity of mixed explosives. Farmer (*Jour. Chem. Soc.*, 1920, cxvii., 1432, 1603) has recently shown that the velocity of decomposition of high explosives becomes greater in presence of another explosive which is more readily decomposed. As far as our experiments go, we are inclined to the view that one chemical change will either promote or induce another chemical change of the same nature.

*Summary.*

(1) The phenomenon of induced reaction is experimentally proved to be of general occurrence.

(2) In oxidation reactions, the phenomenon of negative catalysis takes place when the catalyst is liable to be readily oxidised.

(3) The explanation, of the negative catalysis investigated in these oxidation reactions, seem to stand on the hypothesis of the formation of intermediate compounds.

(4) Experimental evidence has been brought forward in support of the view that one chemical change will either promote or induce another chemical change of the same nature.

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## THE OCCURRENCE OF CALCIUM OXALATE IN THE GIDGEE WATTLE (*ACACIA CAMBAGEI*, BAKER).*

By THOS. STEEL

REFERENCES in literature to the occurence of calcium oxalate in plants are numerous, but records of the amounts present are comparatively scarce. A few of the more important of the latter may be noted. In 1877, W. M. Hamlet and C. R. Plowwright (CHEMICAL NEWS, 1877, xxxvi., 93; *Jour. Chem. Soc.*, 1877, ii., 796) drew attention to the presence of oxalic acid in a large number of fungi, the acid apparently existing in the free state, as hydric potassium oxalate and as calcium oxalate. *Fistularia hepatica* (86 per cent water) contained 0·08 per cent of total oxalic acid, equal to 0·57 per cent in the dry plant, and equivalent to 0·73 per cent calcium oxalate ($C_2O_4Ca+H_2O$)

The presence of the same acid in small amounts in potatoes and malt is recorded by Siewert (*Jour. Chem. Soc.*, 1883, abs. p. 232). Berthelot and Andre (*Jour. Chem. Soc.*, 1886, abs. p. 734) state that they found 13·9 per cent oxalic acid, which is equivalent to 17·8 per cent calcium oxalate, in the roots (dry) of *Rumex acetosa* (common sorrel). Of the 13·9 per cent oxalic acid, 5·9 was in the soluble state and the remainder insoluble.

H. G. Smith (*Jour. Roy. Soc. N.S. Wales*, 1905, xxxix., 23) in a comprehensive paper describes the occurrence of considerable amounts of calcium oxalate in the bark of numerous species of *Eucalyptus*, the percentages present varying from 0·08 to 16·66 of $C_2O_4Ca+H_2O$ in the dry bark.

The occurrence of the same substance in cinnamon and cassia barks was recorded by J. Hendrick (*Analyst*, 1907, xxxii., 14) who found from mere traces up to 3·5 per cent in commercial samples and 6·62 per cent in one of Ceylon wild cinnamon.

J. Otto (*Jour. Soc. Chem. Ind.*, 1912, xxxi., 411) found from 0·4 to 0·9 per cent calcium oxalate in the young needles of pine trees, while old shoots contained 2·3 per cent, and young larch leaves 0·1 per cent, all in the dry material.

R. T. Baker (*Jour. Roy. Soc. N.S. Wales*, 1917, li., 435), as the result of microscopic examination, detected crystals of the same compound in the cells of a large number of Australian timbers.

Further references to various phases of this subject will be found in the collective indices of the Chemical Society and of the Society of Chemical Industry.

F. B. Guthrie (*Agric. Gazette, N.S. Wales*, 1897, viii., 868) recorded an analysis of the ash of the Gidgee or Stinking Wattle (*A. Cambagei*), showing 90·7 per cent of lime (CaO) and 0·40 per cent potash ($K_2O$).

Another sample of Gidgee ash offered commerself in 1898, contained a similar large proportion of lime and small one of potash.

Being struck by the probability of this proportion of lime being due to the presence of unusual amounts of calcium oxalate in the plant, I obtained from Mr. Maiden samples of the timber and bark of *A. Cambegei* and submitted them to detailed examination, with the results following.

I have calculated the oxalate as $C_2O_4Ca+H_2O$, following H. G. Smith, cited above, who found this to be the constitution of the oxalate separated mechanically from Eucalyptus bark. The method of determination used was similar to that described by Smith, with the exception that I ignited the oxalate precipitate completely and weighed as CaO.

*Timber and Bark or Acacia Cambegei.*

(Calculated to dryness).

| | Outer bark | Inner bark | Outer wood (white) | Inner wood (dark) | Average wood |
|---|---|---|---|---|---|
| Ash soluble in acid | 8·48 | 8·43 | 3·28 | 2·53 | 2·86 |
| Sand ... ... 1·15 | 0·44 | 0·00 | 0·00 | 0·00 | 0·00 |
| Potash ($K_2O$) ... | 0·06 | 0·06 | 0·08 | 0·05 | 0·06 |
| Total Lime (CaO) | 7·22 | 7·22 | 2·23 | 1·46 | 1·83 |
| Lime as oxalate ... | 8·20 | 8·16 | 3·08 | 2·46 | 2·70 |
| Calcium oxalate ($C_2O_4Ca+H_2O$) | 18·82 | 18·82 | 5·81 | 3·81 | 4·77 |
| Water in air-dried sample | 8·80 | 9·30 | 9·00 | 9·20 | 9·05 |

These proportions of calcium oxalate in the bark of *A. Cambegei* are the highest I have seen recorded for any plant.

G. Kraus (*Jour. Chem. Soc.*, 1892, abs. p. 1370)

*By favour of the Author, from the Proceedings of the Linnean Society of New South Wales, 1921, vol. xlvi., Part 2, July 27th, 1921.

concludes from the results of experiments on the bark of various trees which contain calcium oxalate in quantity, that this substance constitutes a reserve deposit and is not an excretion, and hat it is redissolved in spring and summer according to the needs of the plant. Branches of *Ribes sanguineum* and other trees varied in their calcium oxalate content with the seasons, the amount present being highest in winter and lowest in spring and summer. The author states that calcium oxalate is certainly liable to solution by long-continued action of an acid circulating liquid like cell sap.

The abstract does not give any details regarding the structure or appearance of the bark examined. I feel more than doubtful about this conclusion. A fall in the oxalate content of the bark during the growing period is more likely to be due to the addition of new bark free from oxalate, than to the solution of the oxalate already deposited. Oxalic acid is usually considered a waste product, harmful to the plant, fixed with lime in order to render it insoluble and harmless, and we know that it is shed in large amount in leaves and bark.

We have seen above that the dead, dry, outer bark of *A. Cambegei* contains the same proportion of oxalate as the inner bark, and even of the latter only a comparatively thin layer may be in metabolic function, in which condition alone it could receive or part with its load of oxalate

Smith (*Jour. Roy. Soc. N.S. Wales,* 1895, xxix., 325); 1903, xxxvii., 107) concluded in the case of *Orites excelsa,* which he found to contain large amounts of aluminium succinate, that the succinic acid was a waste, poisonous metabolic product, fixed by the plant with the only available base forming an insoluble succinate, in order to get rid of it.

To deteremine in how far the barks of other species of *Acacia* resembled *A. Cambegei* in calcium oxalate content, the barks of a number were examined Through the courtesy of Mr. Maiden I was provided with these from the collections in the Herbarium Museum at the Botanic Gardens, Sydney. The analysis of this series was made for me by my colleague, Mr E. F. Vaughan, to whom my thanks are due. All the samples were of mature bark which had become thoroughly air dried.

*Percentages in Acacia Barks*

(Calculated to dryness).

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Total ash ... | 2·01 | 1·56 | 3·05 | 6·80 | 6·14 | 6·05 |
| Total lime (CaO) | 1·64 | 0·91 | 2·63 | 2·54 | 4·04 | 5·60 |
| Lime as oxalate | 0·52 | 0·60 | 1·67 | 2·05 | 2·58 | 3·42 |
| Calcium oxalate ($C_2O_4Ca+H_2O$) | 1·36 | 1·56 | 4·36 | 5·35 | 6·74 | 8·92 |
| Water in air-dried sample | 11·43 | 11·75 | 13·20 | 9·58 | 12·88 | 10·83 |

In the total ash the lime was ignited to CaO.

1 *A. Cheelii* Blakely; 2 *A. adunca* A. Cunn.; 3 *A. auriculiformis* A. Cunn; 4 *A. decora* Reichb.; 5 *A salicina* Lindl.; 6 *A. aneura* F.v.M.

As in the case of the Eucalyptus barks examined by H. G. Smith, there is considerable variation in the amount of oxalate present, but in none of the samples is the high percentage in *A. Cambegei approached.* A variable amount of lime is seen to be in combination other than as oxalate The bark of *A. decora* contained a comparatively large amount of ash insoluble in acid, and was high in iron and alumina, which might be due to admixture with earthy matter, but there was nothing in the appearance of the bark to indicate this.

In a lengthy article on the chemistry of forest trees, by R. Warington in "Watt's Dict. Chemistry" Part I., 1879, viii., 800, a considerable mass of information on the ash constituents of the bark, timber and leaves of trees is collected. A critical examination of this shows clearly that in most of these lime is the predominating constituent, and that there is never sufficient inorganic acid present to fully satisfy the lime and other bases. Throughout the article no specific mention is made of oxalic acid, though it is stated (p. 809) that the carbon dioxide in the ash represents the organic acids with which the bases were originally united, and that the proportion of bases combined in this way is apparently greater in old than in young wood (and bark). In the light of present knowledge, a study of the data given strongly indicates the presence, in many of these timbers and barks, of very considerable proportions of calcium oxalate.

## A NEW CYANIDE.*

By W. S LANDIS

SOME thirty years ago the new use of cyanide in the gold industry brought to the attention of the chemical world the necessity of producing this material on a larger scale than had been previously done, and at the same time of finding cheaper methods of preparation if the compound was to find an extended use. American, French, English, and German chemists attacked the problem most energetically and from their work arose the present-day processes, which, as far as they have become commercially practicable, you are probably familiar.

Two German chemists, working on the barium carbonate process twenty years ago, attempted to supplant the expensive barium salt with a cheaper calcium salt, and obtained a new product, cyanamid, which afterwards formed the basis of development of the well-known "cyanamid process." To a certain extent they were disappointed at the outcome of their work as the new product calcium cyanamid had little in common with the object of their search and after its discovery they sought for many years to convert cyanamid into cyanide. Their first patents on this tranformation of cyanamid into cyanide were taken out eighteen years ago, these patents covering a process of fusing crude cyanamid with common salt in the proportions preferably of one part of cayanamid to two parts of sodium chloride. The mixture of cyanamid and suitable chloride was to be heated to fusion and until foaming of the mass ceased, which operation was reported to require from one-half to one hour. The resulting product was reported to contain cyanide of calcium, but no analyses were given.

* A paper presented at a meeting of the New York Section of the American Electrochemical Society in Boston, April 8, 1920.—*Transactions of the American Electrochemical Society,* 1920, xxxviii.

In attempting to carry out this process on a commercial scale, apparently they met with a great deal of difficulty. I visited their plant in 1914, and found a great many types of equipment had been installed at one time or another, none of which had worked successfully, and the cyanide plant had been closed down and abandoned for some years.

The earliest type of apparatus consisted of a row of iron crucibles set in a gas-fired furnace with the top flush with the roof of the furnace. These crucibles were about 48in. (122 cm.) deep and 20in. (51cm) in diameter and had been made at various times of cast iron, cast steel, and welded soft steels. In operation salt was melted in the pot and cyanamid was then stirred in and the whole mass kept fused for a suitable length of time. The transformation efficiencies were extremely low, but no actual record of the same was made public.

The next development consisted in setting two iron crucibles side by side in the furnace. In the one crucible they charged salt and melted it, and in the second they charged cyanamid and heated the same to redness. Molten salt was ladled from the first crucible to the second crucible, and when a proper quantity had been added the whole mass was kept melted until by chemical analysis the maximum yield of cyanide had been attained. The contente of the pot were then ladled out and cast into slabs.

The enormous amount of hand labour involved in this operation rendered it commercially impracticable, and a new equipment replaced the old. A revolving furnace was constructed with an enlarged melting hearth midway between the tires. Salt wa smelted in this hearth and tapped into an iron ladle and conveyed to a crucible containing red-hot cyanamid. This operation was also unsuccessful in that there was very considerable wear and tear on the salt melting furnace, and further great care had to be exercised in pouring the molten salt on to theheated cyanamid, as the initial reaction was verv violent and the pot frequently boiled over.

The maintenance of the externally heated crucible at the required high temperature became quite burdensome, and a new type of furnace was developed in which an iron pot, provided with a spout, was set into a fuel-fired furnace. This pot was built of welded flange steel. It was 3ft. (0·92 m.) deep and 2½ft (0·76 m.) in diameter. There was also provided an electrode 5in. (12·7 cm.) square and hung on a chain block in line with the axis of the pot so that it could be lowered into the fused mass contained in the same. In this way a single-phase furnace using about 40 volts and 1200 amperes was made in a setting also provided for initial fuel firing. In operating cyanamid was charged into the bottom of the pot and heated to redness by the fire underneath. Salt was melted in the rotating furnace above described, and was slowly poured into the electric furnace at such rate that no very violent reaction ensued. The carbon electrode was then lowered, the current turned on, and the whole mass kept heated electrically until the reaction was complete. The cyanide was tapped through the spout and cast into slabs.

This furnace and process was not successful—the efficiency of nitrogen transformation was very low and the final product contained a comparatively small percentage of cyanide. I was informed, however, that the same type of furnace was successfully being used in another part of Germany, where the salt was melted electrically, and there was being turned out in this second plant a grade of product containing 40 per cent equivalent potassium cyanide at an efficiency of nitrogen transformation of over 90 per cent. I accordingly visited this other plant, and was very much surprised to find there an entirely different type of apparatus in use.

At this second place I found they had tried the combined fuel-fired and electric furnace just described, and had come to the conclusion that the uneven distribution of electric energy throughout the bath caused very uneven heating of its contents, and which was believed to be the cause of the very poor efficiency obtained from the process The iron pot would only last two or three runs before cracking, and they had abandoned this type of apparatus for a resistance type of electric furnace built of brick. This improved furnace was of the tilting type with a rectangular hearth and arch roof and lined with magnesite brick. The side walls were formed of carbon blocks and electrically connected with a source of current. In practice these blocks were short-circuited with a rod of carbon, and salt was thrown into the furnace and melted around the rod, thus establishing a path of current between the side electrodes. The furnace was then filled with salt. Cyanamid was then added to the melted bath and the heating continued until by chemical analyses the maximum content of cyanide had been formed, when the molten bath was poured out and cast into slabs. I witnessed several operations of this furnace, and found that the furnace produced about 400 kilogrms. of molten product in from three to four hours. The apparatus used about 21 volts and 2800 amperes. The equivalent potassium cyanide in the final product ran from 8½ to 17½ per cent in the various runs and the nitrogen transformation efficiency from 40 to 75 per cent. During the last run I witnessed, the furnace became blocked with a white spongy material, and all operations were abandoned.

It is thus apparent that in the 15 years elapsing between the initial experiment and my visit the Germans had been able to do little or nothing with the process of transforming cyanamid into cyanide. They had tried out many types of furnaces none of which were successful in any marked degree and had produced only a small amount of product of comparatively low grade and at great inefficiency. They were firmly convinced that it would be necessary to use more than two parts of salt to one part of cyanamid in order to make reaction take place at all and that for smooth working at least three parts of salt to one of cyanamid was absolutely necessary, also premixing of the charge was wrong chemically and must not be used. On the basis of these mixtures the final product should test between 15 and 20 per cent of equivalent potassium cyanide. There were many theories and ideas advanced on the subject, but I could find no comprehensive chemical study of the process and little information of scientific value. In fact, the outlook for this transformation was most discouraging.

In the late fall of 1916 there was a sharp advance in the price of cyanide in this country, and a great shortage in the available supply. The gold and silver mills of the Continent faced a serious situation, and finally one of the large users of the material came to the American Cyanamid Company with a request that it endeavour to co-operate in producing the necessary requirements of this material. With the discouraging report on the German process in hand, and no time available for experimental work, the outlook was not particularly bright, but the problem was attacked and a plant was designed and equipped using resistance furnaces of a modified design, and the older German procedure was altered somewhat with the hopes of obtaining at least results as good as the Germans had anticipated.

This plant was put into operation at Niagara Falls late in December, 1916. It was provided with five resistance furnaces of a tilting type, and two salt melting furnaces of fixed type. While completing the salt-melting furnaces, the resistance furnaces were put into operation as combined salt melting and reaction units. They were very much larger than the German furnaces, and the design and construction was quite new. They functioned extremely well as such furnaces go, considering the complicated operation The time of an operation, including salt melting and reaction, was reduced to about 2½ hours, and the salt-melting furnaces were never used for their intended purpose.

Salt, charged cold, was first melted in the furnace by adding directly to the hot furnace, the heated walls conducting sufficient current to start the melting. Into this bath of molten salt cyanamid was fed by hand, stirring up the bath with an iron rod, and as soon as all the cyanamid was in, the furnace was tapped by pouring into chill cars. After cooling, the cake was broken up and loaded into caustic soda drums which formed the shipping container of the final product. Later it was tapped directly into the shipping drums.

The process was somewhat troublesome to carry out. The life of the low-grade magnesite brick lining, the only kind then obtainable, was at most six weeks. It then became so conducting, due to the iron content of the bricks being reduced by the cyanide and through its absorption of the cyanide itself, that relining was necessary. Further, the addition of the cyanamid had to be slow and cautious as considerable foaming took place during the reaction and the contents of the furnaces would frequently boil over. The first great improvement was the discovery that the addition of a very small amount of calcium carbide to the furnace would entirely stop the foaming. This permitted the cyanamid addition to be made very quickly and the power input was, therefore, increased to obtain the additional melting speed. I had learned in Germany that the furnace men over there were of the very fixed opinion that at no time should the temperature of the bath rise above 960° C., or decomposition of cyanide would result Due to an accident to the electrical system at Niagara, one of the furnaces received an undue amount of electrical power in one of the runs, and the temperature shot up several hundred degrees above the limit set by the Germans, yet most excellent results were obtained. All furnaces were, therefore, operated at the highest possible temperature, and as a result within three months of the starting of the plant the Cyanamid Co. not only maintained a daily production rate of nearly four tons of sodium cyanide but had carried on experimental work which had enabled it to dispense entirely with the salt melting furnace, as well as some of the reaction furnaces, to cut down the time of reaction to half, to avoid foaming, and further to increase the test of the finished material up to approximaely 24 per cent. equivalent sodium cyanide.

The unsatisfactory performance of hte tilting furnace led the Cyanamid Co. to experiment with a new type using a suspended electrode and the combination arc-resistance method of heating. The success following this development enabled it to abandon the numerous small resistance furnaces and concentrate its eorts in a single unit and at the same time to obtain a very greatly improved product. After a short period of development there was constructed at Niagara a singe-phase furnace with conducting hearth and containing a single suspended electrode and which furnace starting with an initial capacity of some 10 to 12 tons of product per day running about 28 per cent sodium cyanide equivalent, is now operating at nearly 30 tons of product per day, averaging 42 per cent equivalent sodium cyanide. Additional furnaces are in process of construction.

The development of the industry has been quite rapid. In 1917 there was produced approximately 2,187,000lb, equivalent to 100 per cent sodium cyanide. In 1918 this grew to 2,350,000. In 1919 a very considerable revision of the process and equipment was made, and as a consequence the plant operated only seven months, during which period it produced at the rate of over 4,000,000lb. of NaCN per year. aThe quality of the product started at about 14 per cent equivalent sodium cyanide in January, 1917, and in August, 1919, ran uniformly between 36 and 37 per cent equivalent sodium cyanide. Material running as high as 50 per cent equivalent sodium cyanide has been produced and there have been shipped several carloads running around 45 per cent, of which I shall speak more later.

The process and apparatus used for manufacturing this product has been extensively described in the many United States and foreign patents covering the process. Essentially cyanamid, salt and calcium carbide are mixed together and continuously fed to a single-phase furnace designed so that it has a very small cubical capacity as compared with the power input. Melting is extremely rapid and the fused product is removed from the furnace almost continuously to a cooling device which instantly chills the product. This is necessary to prevent reversion of the initial reaction, whereby calcium cyanamid, plus its contained carbon, is converted into cyanide. The proportions of cyanamid and salt vary with the product to be made.

In 1917 operations were started with two parts of salt to one part of lime nitrogen and gradually decreased in salt content until in making the present standard 42 per cent product more cyanamid than salt is being used. The large furnace has been successfully operated with proport ons as low as two parts of cyanamid to somewhat less than one part of salt, and the experimental furnace with no salt whatever.

The resulting product is marketed in the form of small, thin scales of a greyisn-black to shiny-black appearance, and the standard grade known as Aero Brand Cyanide "Grade X" contains between 36 and 37 per cent equivalent sodium cyanide. This method of expressing its composition is used because it is sold on the basis "per pound of sodium cyanide equivalent." A constitutional analysis of the material has so far proven impossible of execution, but evidence points to the fact that it consists of a mixture of calcium cyanide, sodium chloride, and free lime with fractions of a per cent each of calcium carbide, calcium cyanamid, and other minor impurities obtained from the ash of the coke used in cyanamid manufacture. The product known as Aero Brand Cyanide "Grade XX" contains 45 per cent equivalent sodium cyanide—the cyanogen being actually present as calcium cyanide—a slightly higher percentage of free l me and a materially lower percentage of salt than the X grade.

As to the use of this material it has found an enthusiastic reception in the mining industry. Being made from cyanamid, one of the cheapest forms of combined nitrogen, and common salt, its cost of manufacture and its selling price are materially less than the purer forms of cyanide hitherto on the market. The use of caustic soda drums for packing has cut down the expensive item of metal containers forced upon the early industry.

The first Aero Brand cyanide made in 1917 went into the precious metal industry after a short series of laboratory tests in which it was demonstrated that it would dissolve gold and silver with equal efficiency to the 98 per cent grade then in the market, and that the accumulation of soluble salts due to the cyclical use of solutions in the mill would not prove troublesome. In mill scale operations the drums were opened up and the cyanide placed in a revolving tumbler which dissolved it in water, thus giving an opportunity for any acetylene produced to be evolved outside of the mill solutions. Containing as it does a small amount of insoluble material, part of which is carbon, difficultly with precipitation due to the presence of this carbonaceous material was feared, and the solutions were therefore filtered before passing into the mill circuit. Experimental work quickly determined that the carbonaceous residue had no precipitation effect upon cyanide solutions of the precious metals and this early practice of pre-solution was quickly abandoned and from thence to the present time Aero Brand cyanide is dumped directly into the mill circuit.

The presence of a small amount of sulphur in the cyanamid is carried through into the Aero Brand cyanide as a sulphide. Difficulty was feared with the presence of this sulphide, but several years' experience has shown that the aeration as employed in the cyanide mills quickly oxidises these sulphur compounds and renders them harmless As a result no trouble has been experienced from its sulphur content.

In the gold industry, where the cyanide consumption per ton of ore is comparatively small, no difficulty has ever been experienced with the accumulation of soluble salts. In the silver industry, where cyanide consumptions of not over five pounds equivalent potassium cyanide per ton of ore is experienced, they have similarly had no trouble from accumulation of the soluble salts, but where consumptions are considerably above that figure, certain difficulties have made themselves shown in several of the silver mills. The calcium chloride obtained from double decomposition of calcium cyanide and sodium chloride acts as a precipitating agent and greatly assists in the settling of the mill solutions. Its accumulation in such a solution, however, to an undue extent, particularly in the case where cyanide consumptions run from 10 to 100lb. per ton of ore or concentrates leads to a decrease in the available alkalinity of solutions, and steps have had to be taken to eliminate it. These steps consist in the addition of any simple precipitating agent for lime, the precipitated lime being removed in the filter with the mill tailings.

In every case, either in the laboratory or in the mill, the cyanogen content of Aero Brand cyanide has proven itself equally as efficient in the extraction of precious metals as that of the 98 per cent sodium cyanide pound for pound of contained cyanogen, added to which are the advantages of a considerably lower cost, slight alkalinity of the Aero Brand cyanide, and the marked influence on the rate of settlement of the solution. The new product has found a most favourable reception in the industry and is very widely and extensively used to-day. In the gold mills it offers no problem in handling and causes no difference in the practice beyond the fact that the making up of a stock solution is not considered as good practice as the dumping of the cyanide directly into the barren solution along with the ore. In the silver mills, using a considerable quantity of cyanide per ton of ore, simple precipitating methods for eliminating accumulated lime are in use, otherwise their practice is in no way affected.

In its present state of development Aero Brand cyanide is not adapted to use in the case-hardening industry or in electro-plating. For the case-hardening industry is is very questionable if it has anything to offer in the future, but in the electroplating industry steps are being taken to perfect a method to simply convert it into forms such as the electro-plater can conveniently use, and it will undoubtedly make some headway in that industry.

For the preparation of cyanides it is a simple matter to dissolve Aero Brand in water, adding sufficient soda ash to eliminate the lime and filter. It is then ready for precipitation of the various insoluble cyanides.

For the preparation of ferro-cyanide it is very satisfactory. A solution of ferrous sulphate is made up of suitable strength and into this is dumped an equivalent amount of Aero Brand cyanide and the mass agitated for a short time. Quantitative transformation of the cyanogen in Aero Brand to ferro-cyanide readily takes place. The insoluble material left in the treatment vat is filtered off, the filtering operation not being very complicated, but the amount of cake to be handled is considerable. The resulting ferro-cyanide is then concentrated and at a certain density about 95 per cent of it will separate out as a meal and the other 5 per cent will remain behind in solution with the chlorides of calcium and of sodium. The meal is separated in a salt filter attached to the evapprator and the solution is thrown away. Recrystallisation of the meal with return of mother liquor to the original treatment tank yields a

sodium ferro-cyanide of remarkable purity. The transformation can be accomplished with not over 5 per cent loss of cyanide.

Recently the manufacture of anhydrous prussic acid from the crude cyanide has been successfully undertaken. Into an acid-proof generator Aero Brand cyanide and water is charged, the apparatus closed up and sulphuric acid run in. A considerable evolution of prussic acid gas takes place and the solution in the generator is finally cleared of all prussic acid by the admission of live steam. A brine-cooled condenser liquefies the gas evolved from the still and condenses an impure acid containing about 80 per cent prussic acid. This is charged into an iron still and re-evaporated, the resulting condensate being about 98 per cent pure, in which state it is used in fumigating in the citrus growing districts. The resulting liquefied product is water white and practically chemically pure, at most containing only the most minute traces of foreign products. The construction and operation of the liquid gas plant, as the same is called locally, has been a most successful operation in every way, the only regret being that the installation was not about three times as large as originally planned because of the great demand for the high quality material it has turned out.

There is no reason to doubt that Aero Brand cyanide will find a place in many other chemical industries as up to the present time practically no limitations in its use have been found and no chemical properties which prevent its utilisation in the many cyanide derivatives. Quite recent developments have shown the feasibility of manufacturing the higher-grade product containing above 45 per cent equivalent sodium cyanide. These developments are too new to present at this time. A discussion of the process or of the use of the resulting product, which has several new characteristics will be reserved for the future.

### *Conclusions.*

The development of the process of transforming cyanamid into cyanide marks another triumph of the American electrochemist. We accomplished more in a few months than the foreign chemists accomplished in 15 years. Three months after starting the designs of a plant our American chemists were producing to the extent of four tons of equivalent sodium cyanide per day of a much higher grade than the Germans had ever hoped for. Within a year we had reduced our operation to a single small electric furnace of a continuous type and produced a product of higher cyanide content than the Germans ever thought possible and at a nitrogen efficiency of over 90 per cent.

The resulting product of uniform quality and excellent physical characteristics has found a very increasing market in the various industries using such a product and is to-day pushing the pure high-grade product steadily out of its long entrenched fields. For the present year the outlook is for a consumption of Aero Brand cyanide equivalent to nearly 5000 tons of 100 per cent sodium cyanide With further development along the lines of transforming this material into its many other derivatives, particularly in view of the very low cost of the raw materials entering into its manufacture, and the simple apparatus and process used, we confidently look forward to cyanide made from cyanamid dominating the world's cyanide market.

## VENTILATION AND HUMAN EFFICIENCY.*

(Concluded from page 310.)

In Scotland the majority of the lamps were the little miners' lamps for which Englishmen as a rule had a strong contempt, but, notwithstanding the contempt, he was glad to see that a patent lamp of the kind was coming into favour in England. Therefore, the English colliery manager had to thank the Scotch colliery manager at least for giving him that tip. The further they went into the works the more the air became contaminated, and the men at the end were undoubtedly swallowing very bad air That was a matter which they could not possibly help, and the only cure for it was, as Dr. Haldane had said, by sending a large current of air to sweep through the colliery workings.

A good deal of discussion had been started, particularly in Scotch coal-fields, with regard to obtaining fresh air at the faces, and the question whether or not it could be done by the existing method of providing ventilation from the surface alone, by which he meant having a suface fan with a good-sized down cast shaft and a good-sized up cast shaft, or whether it was better to have auxiliary fans underground. Some managers declared that by having auxiliary fans, the air was cooled. He was not so sure about that, but some mangers held that the air that came from an auxiliary fan placed underground was much cooler than when the whole air came right in from the surface and went right back from the one fan. That was a question that Dr. Haldane might take up, if he had time, and settle the knotty point.

The paper he thought was of great value to mining engineers, and he only regretted that all members of the Institution of Mining Engineers did not have the opportunity or reading it. If some arrangement could be made whereby such papers read before the Institution of Mining and Metallurgy could also be discussed by the Institution of Mining Engineers, he thought it would help both Institutions and the Industry generally.

He desired to thank the President and members for permitting him to contribute to the proceedings, and he had also to thank the author for his excellent paper, which he had thoroughly enjoyed.

Mr. Bernard W. Holman said that he was sure they were all very grateful, as mining engineers, to Dr. Hill for having brought that instrument before the Institution, and for having explained it so clearly. It now behoved the mining engineering profession to test it themselves and find out how far it could actually be employed usefully in the mines.

One of the first things that occurred to one was its use for testing the efficiency of booster fans underground. An instrument which actually gave the cooling power per unit of surface seemed peculiarly fitted for testing whether the increase of air velocity obtained by booster fans gave an increase of cooling power commensurate with the additional amount of money spent.

It was possible to test a man's efficiency by the

* Discussion before the Institution of Mining and Metallurgy, October 27, 1921.

katathermometer in conjunction with an ergometer which gave actual measurements of how much work the man put out. To begin with, as the Mine Rescue Apparatus Committee had shown very clearly in their report, the instrument not only showed what output the man was capable of, but it also showed his stamina (suitability for sustained effort), and his fitness. By finding out what his efficiency was they could find out how far his output could be improved They all knew that in Africa and other places it had been necessary to employ new classes of natives and other workers underground. The only practical method of testing them was to measure their output and to see how much the death-rate turned out to be per thousand per year. Obviously sometimes such tests had to be stopped because the death-rate would be too high. Such a method was troublesome and expensive. Efficiency tests on individuals would be far more convenient and much cheaper. It could be tried in practice whether this method of testing the suitability of men for working underground gave reliable results.

Then there was a third use which remained to be tested by mining engineers, and that was the effect on output of the general conditions of the mines. The man's efficiency could be tested at different depths, temperatures, and humidities. There was also the peculiar question of optimum effort which Dr. Orenstein was going into so fully, i.e., whether it was better to let a man work very hard and then have a rest, or whether it was better to let him have one or two or three rests throughout the shift, and what was the best length of shift. That was a test for which the katathermometer happened to have a particularly useful scope. They had been so much in the dark before with regard to the influence of cooling effect on a man that a good deal had had to be held over.

With regard to the recommendation of the ergometer he felt that it was a matter of opinion rather than a statement of scientific fact that efficiency depended on cooling power; efficiency should be measured. They had heard he statement made that the cooling power was the measure of efficiency, and that the cooler the air was the higher the efficiency of the man. Any statement connected with human efficiency and the human machine ought to be treated really as an empirical one, because they knew very little even about the process of oxidation in the tissues. To quote a President at the last Meeting of the British Association: "We do not know how it is done, and we cannot do it ourselves." He (Mr. Holman) almost thought that applied to such a simple thing as digestion also. Therefore they had these factors: cooling power, comfort, and efficiency. They were three different things; although they were undoubtedly connected they were not necessarily equivalent. It was interesting to note the very elaborate experiments which had been carried out by the French Army recently to test new recruits joining the Army in order to see how far and with what loads they could march, and how on a forced march a rest of ten minutes per hour, or five minutes per hour, or no rest at all, affected the efficiency of the men. It seemed to him that in precisely the same way that instrument could be used to test the real capability of a new man presenting himself for work. When the fuel consumption side of the instrument was simplified slightly, presuming the man would submit to it and that his Union would let him, it seemed to him that it would be possible to test a man's actual physical efficiency for work before engaging him.

The effect of alcohol had been very carefully studied by means of the ergometer, also the amount of energy used, and the conditions of efficiency of workers in various industries, even including men hewing coal, had been already investigated by Prof Waller.

It was very interesting to see the amount of modification in the revised formulæ of Dr. Hill. He (Mr. Holman) rather doubted their absolute validity when he saw them at the previous meeting because he had not been quite able to see how the cooling power varied with the root of the velocity. When they dealt with rather higher velocities for air-cooled engines for aeroplanes, the cooling power appeared to vary directly with the velocity. In the army they had to make allowance for shell-fuses burning more quickly when the shell was going through the air than when it was on the bench being tested. In that case there was actually a heating effect owing to increased velocity and not a cooling effect at all. He would like to ask Dr. Hill what absolute methods of checking low velocity he had, and whether he used any kind of hot wire anemometer, *e.g.*, that of Dr. Vessot King, or whether he put a given quantity of heat into the wind tunnels and calculated in that way. For high velocities pressure measurements were sufficient.

There was one point on p. 2 with regard to the organic poisons in the exhaled air and the supposition of the existence of such being negatived by exact experiment. They all knew how continued insanitary conditions appeared to breed fever in the past. He would be very much obliged for references to any experiments on human beings in that connection. They all knew about the experiments on guinea pigs, which could almost live without any ventilation at all, and even live with carbon monoxide for quite a long time. He would be very glad of any references to prolonged experiments on men which dispelled that ancient "superstition" about exhaled air.

With regard to Dr. Hill's statement on p. 2 that high cooling power improved the circulation of blood and caused "better appetite, digestion and absorption of food and that constipation is avoided," he (Mr. Holman) thought that all those things were very often constitutional. From his own experience and observation appetite was quite a constitutional thing, and often independent of body weight. He thought, therefore, that such things being largely constitutional varied far more with the individual than they did with katathermometer readings.

Mr. H. K. SCOTT said that Dr. Haldane, in determining the measure of atmospheric conditions suitable for the efficiency of workers, had stated that at 80° F. wet-bulb, the work of a miner falls off, and at 85° F. hard work is scarcely possible.

At the Morro Velho Mine of the St. John del Rey Mining Co., in Brazil, however, the temperature in the stopes on more than one occasion last year actually reached 90° F. wet-bulb, and unless

some method had been evolved of reducing this figure, further excavation in depth would have been impossible. As a result of the installation of a cooling plant, which has been in operation there since last December, the temperature fell appreciably, and three months later, the thermometer nowhere registered more than 83° F. wet-bulb in the mine.

The cooling plant has been worked to bring about a very gradual fall in temperature, in order to prevent blistering of the rock, but Mr. Scott was informed that at the present time men were working underground wih their coats on. This appeared to him a very satisfactory result, inasmuch as the improved conditions would prolong the life of the mine, as well as reduce sickness and tend to prevent industrial unrest.

This result has not been achieved without large expenditure, which, he understood, approached two hundred thousand pounds This figure, however, included the provision of power, in addition to that of the cooling plant proper. The incidence of the War, and the fact that the installation was a pioneer one, no doubt resulted in the expenditure being so great.

The author suggested that by adjusting the cooling power to the heat production of the worker, sweating could be prevented, and the work done with comfort and ease.

He (Mr. Scott) would ask Dr. Hill if, in his reseaches, he had taken into consideration the fact that men do not all sweat at the same temperature and with the same physical exertion. He presumed that an average figure had been taken which would probably give a satisfactory result in factories, but he was afraid that, although in deep mines improved ventilation make work more tolerable, the environment would not permit such ideal conditions as the author postulated.

The President said that he felt sure that the members would all join with him in passing a hearty vote of thanks to Dr. Hill for his very interesting paper, a paper which, although a theoretical one, was of great interest to practical men because it was through scientific men bringing these things forward that practical men were enabled to adapt them to their particular conditions and make them of practical use.

*Contributed Remarks.*

Mr. H. F. Collins: It seems to me that the katathermometer is nothing but an improved form of wet-bulb thermometer *plus* a time factor; what it measures is simply the evaporative power of a current of air. If this be so, the same result ought to be measurable by noting the difference between the dry and wet bulb temperatures, and the time taken by the wet bulb to reach this difference, which ought to be standard for each given set of conditions. A factor can then be worked out for converting the readings of any wet-bulb thermometer into kata degrees.

There are cases in which the indications of a katathermometer, graduated only from 100° down to 95°, would be of no value, for one often finds—especially in tropical countries—working places the temperature of which is above 100° F On two occasions in the writer's life it has been his lot to visit working places the temperature of which (from special causes in each case) exceeded 130° F. For such conditions the kata would be useless, whereas our old friend the wet-bulb, the readings of which had been standardised against a kata, could be employed successfully.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

*November* 24, 1921.

Prof C. S. Sherrington, President, in the Chair.

The following papers were read :—

(1) *"Observations on Reflex Responses to the Rhythmical Stimulation in the Frog."* (2) *"The Effects of Constant Galvanic Currents upon the Mammalian Nerve-muscle and Reflex Preparations."* By K. Sassa.

(1) The object of the investigation was the study of the relation between the frequency and intensity of stimulation and the resulting reflex reactions.

It was found that there is an optimal intensity when the rate of stimulation is rapid, but not at moderate rates. There is also an optimal rate for any given intensity. The reflex contraction evoked at optimal rate of excitation is often nearly as powerful as the direct one obtained by similar stimulation, especially in the first period of contraction.

(2) This communication gives the results of a study of the reflex effects resulting from stimulation by constant galvanic currents applied to an afferent nerve of the hind limb.

The main points of enquiry have been: (1) the relation between reflex excitation and inhibition of the decerebrate tonus of the vasto-crureus; (2) whether the "excitation formula" (Pflüger's law) holds good in mammalian afferent nerves; and (3) whether there is continuous excitation during the passage of the current through an afferent nerve.

*"The Hæmolytic Action of Sodium Glycochocolate."* By E. Ponder.

In this paper it is pointed out that the hæmolytic power of sodium glycochocolate is greatly increased by the addition of small amounts or histamine or histidine.

The effect produced by such a mixture on freshly prepared erythrocyte suspensions differs from the effect produced on supensions which have been standing for some time. Erythrocytes can be rendered immune to the hæmolysis produced by mixtures of sodium glycochocolate and histamine by the previous addition of histamine to the suspension.

It is suggested that the hæmolysis is due to changes of surface tension.

Tables illustrating the phenomena are given.

*"The Titration Curve of Gelatine."* By Dorothy J. Lloyd and C. Mayes.

Hydrochloric acid combines with gelatine in solutions whose acid concentrations are less than 0·04 normal, according to the law of mass action. $K_b$ for gelatine is $4{\cdot}8\times10^{-13}$ if 839 be taken as the reacting weight of gelatine.

The theory is put forward that over this range of the curve of combination of gelatine with

hydrochloric acid, the combination occurs at the free—$NH_2$ groups. These groups are present in the lysin, arginin, and possibly some other of the amino-acids of the gelatine

In dilute sodium hydroxide of a concentration less than 0·01 normal, the gelatine combines with the base less rapidly than would follow by a calculation from the value for $K_b$ and the value for the iso-electric point, if 839 is taken as the reacting weight.

It is suggested that the number of positions of attachment for bases is not the same as the number of positions for acids, *i.e.*, that the reacting weight $= \frac{\text{molecular weight}}{\text{basicity (or acidity}}$ is not the same in acid and alkaline solution.

*"Idio-Ventricular Periodicity."* By D H. DE SOUZA and J. A. HEWITT.

A perfusion experiment on the excised heart of a frog is described and discussed, in which periodic grouping occurred as an independent ventricular phenomenon.

## SOCIETY OF PUBLIC ANALYSTS.

*Ordinary Meeting, December 7, 1921.*

Mr. ALFRED SMETHAM, President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. John Leonard Lizius, B.Sc., A.I.C., Harry Malkin Mason, M.Sc. (Sheffield), F.I.C., Thomas McLachlan, A.I.C., Charles March Caines, F.I.C., and Girija Nath Mukerjee, B.Sc. (Cal.).

Certificates were read for the second time in favour of Messrs. Jack Cecil Drummond, D.Sc. (Lond.), F.I.C., Alfred William Long, John Charles Mellersh, Charles Harold Wright, M.A. (Cantab.), F.I.C.

The following papers were read:—

*"The Estimation of Small Quantities of Antimony in Copper and Brass."* By B. S. EVANS, M.B.E., M.C., B Sc., F.I.C.

The author states that existing methods are unsatisfactory, either on the score of length or accuracy, and puts forward a process which he claims to be reasonably rapid and accurate. The method is described in detail, the copper being first eliminated with sodium hypophosphite and the antimony precipitated on copper foil, from which it is dissolved and re-precipitated as the sulphide, and estimated colorimetrically. The chemistry of the process is dealt with, and the factors governing the Reinsch and hypophosphite tests for arsenic discussed.

*"The Inks of Ancient and Modern Egypt."* By A. LUCAS, O.B.E., F.I.C.

The author refers to the types of pens used in ancient Egypt and gives an account of the black and coloured inks on ancient papyri and parchments. The chemical reactions of these inks are described, and an analysis is given of a carbon ink of the sixteenth century, B.C. The inks in old Arabic and Coptic books are next described, and evidence of the use of iron inks in papyrus MS. of the seventh century A.D. is adduced. The composition and characteristics of modern Egyptian inks are outlined and analyses of different qualities of carbon inks are given. Finally the question of the brown discolouration of ancient carbon inks in MS. and books is discussed and explained.

*"Notes on the Analysis and Use of Red Squill in Rat Poisons."* By C. L. CLAREMONT, B.Sc., F.I.C.

Red squill (*Urginea Maritama*) is described, a short *resume* of previous work given, and methods of using as a raticide explained.

The author gives analyses and toxic values of a number of red squill powders, the main feature of which is the presence of a sugar-like substance which serves as an indication of the presence of squill, and gives approximate quanti-relationship results, but it does not appear that there is any relationship between this and the toxic value. Similar figures derived from the white squill (B.P.) and *Urginea Burkei* are also given and the difficulty of distinguishing red from white squill dealt with. Analyses of liquid extracts of a squill and other rat poisons containing squill are given, and experiments are described bearing on the best method of making squill preparations.

# NOTICES OF BOOKS.

*Aids to Chemistry.* By WILLIAM PARTRIDGE, F.I.C. Pp. viii.+280. London: Baillie, Tindale & Cox. Price 6s. net.

This little book is intended for the use of students who have already been through a course of chemistry, and have therefore had some experience in practical work. The object of the text has been to recall and explain to the reader the various reactions he has encountered in his laboratory work, and to act as a handy book of reference.

After an introduction dealing in a general way with the science of chemistry, and the indestructibility of matter, short paragraphs are devoted to compounds and mixtures, synthesis, and analysis.

A chapter is given to optical chemistry and the use of the spectroscope, and then the subject of the non-metallic elements, their occurrence, history, and reactions, occupy some 50 pages, while the remainder of the book deals very practically with the quantitative analysis of compounds and the chemical nature of the hydrocarbons.

Naturally, when embracing such a range of subjects in a small book, the matter is very condensed, but as an aid in recalling the mind to work that has been done in the laboratory the book will no doubt be found of value to medical, veterinary, and pharmaceutical students. A list of the elements with their symbols and approximate atomic weights is given at the end of the book, and there is a general index.

*A Handbook of Laboratory Glass-Blowing.* By BERNARD D. BOLAS. Pp. vi.+104. London: George Routledge & Sons, Ltd. New York: E. P. Dutton & Co. Price 3s. 6d. net.

This handy and clearly illustrated booklet is devoted to the subject of such glass-blowing as is generally encountered in laboratory practice. It is quite evident by the descriptions and illustra-

tions given that the author is writing from a very practical point of view. By closely following the directions and the use of a plentiful amount of patience, it should be quite possible for the student with average manipulative skill to become sufficiently proficient to enable him to manufacture for himself nearly everything that is needed in the laboratory.

In addition to glass-blowing, many dodges useful in the laboratory are given, such as drilling and grinding glass, calibration and graduation of glass apparatus, manufacture of thermometers, spinning glass, and the making of Sprengel air pumps, and illustrations are given of the method of making the extremely complicated Geissler tubes that were to be seen in every optician's shop years ago.

This is a book that we should strongly recommend to all workers in science, especially chemical students.

*An Introduction to Zoology for Medical Students.* By C. H. O'Donoghue, D.Sc., F.Z.S. Pp. x.+501. Price 16s. net.

The object of this imposing volume is to provide a textbook for the zoological portion of the syllabus in biology for the first examination for medical degrees in the University of London.

An introductory outline is given to the probable theories relating to heredity and evolution, and it is pointed out that no course in zoology can be considered adequate unless the reading is accompanied by practical work. No pains have been spared to fully illustrate the work by both half-tone plates and diagrams.

We are rather surprised that little or no reference has been made to the application of X-rays for the investigation of osteological structure. It was thought in the early days of Roentgen's discovery that the method would be found of value. It may be that the science of radiology has developed in a direction that makes it difficult for the zoological student to avail himself of this valuable means of research.

*The Spectroscopy of the Extreme Ultra-Violet.* By Theodore Layman, Ph.D. Pp. 132 London: Longmans, Green & Co. Price 5s. net.

This work is one of the series of monographs on physics, edited by Sir J. J. Thomson, O.M., F.R.S., and Frank Horton, D.Sc., M.A. The author in his preface states that the book might well have been called the Spectroscopy of the Schumann region. The work of the late Victor Schumann will always be remembered by spectroscopists in connection with the exploration of the spectrum in the extreme ultra-violet. The excessive care which he took in every detail in the construction of apparatus and the magnificent results that he obtained really laid the foundation for the research in this important field. Professor Layman's work on the subject is well-known.

Part I. deals with the photometry of ultra-violet and the absorption of solids and gases. Chapter II. begins with the description of the apparatus used in the investigation of the ultra-violet. This portion is very clearly illustrated, and diagrams of the vacuum spectrograph are given. On page 54 a description is given of Schumann's photographic plate, having the remarkable property of being very sensitive to the extreme ultra-violet, but quite insensitive to light of greater wave-length than A U. 3000; the shortest wave-length obtained by the direct method appears to be in the neighbourhood of 900 A.U.

As it has now been established that X-rays are a form of ether vibration of wave-lengths in the neighbourhood of one and two Angstrom units, the gap between the X-rays and the shortest ultra-violet radiations is still of absorbing interest, and the author thinks that it will probably necessitate a considerable change in the methods of investigation if the gap is to be successfully bridged. Work in this direction is stated to have been carried out by Dember, who produced X-rays by the bombardment of photo-electrons of low speed of an estimated wave-length of 475 A.U.

Tables of wave-lengths in the ultra-violet spectrum, of hydrogen, nitrogen, argon, aluminium, gold, and some other elements are given, and in an appendix at the end, Schumann's method of preparing the photographic plate and the developer is described.

*The Formation of Colloids.* By The. Svedberg, Professor of Physical Chemistry in the University of Upsala. Pp. 125, with 22 Illustrations. London: J. & A. Churchill. Price 7s net.

Professor Svedberg's name is well-known in connection with the subject of colloids, and it is with very great pleasure that we are able to announce that he has undertaken the publication of a series of monographs upon the subject. It is proposed by this method to keep up to date with this rapidly growing science. Professor Svedberg, in his preface, refers to the help he has received from Emil Hatscheck, whose name is also well-known in this connection.

The first of the series now before us gives a survey of the processes which cause the formation of colloids. In his introduction, the author gives full credit to the labours of Thomas Graham, whose experimental investigations laid the foundation of the science of colloidal substances. Since those days, many investigators have devoted themselves to researches in this fascinating field. The names of Linder, Picton, Zsigmondy, and Ostwald, will always be associated with the pioneer work that has been done on the subject Ostwald has referred to the colloids as "the world of neglected dimensions" because of the lack of interest which, until very lately, caused them to be a disregarded field of study.

The first paper in the monograph is devoted to the formation of dispersed systems in vacuo, and deals with the metallic deposits on glass and other surfaces. There is a critical temperature for every element, above which the molecule instead of adhering to is reflected from the surface. This temperature for mercury is about minus 135° C., and for silver plus 575° C.

The formation of mercury mirrors upon cooling a globe containing mercury vapour is familiar to all frequenters of the Royal Institution of London by the classical experiments of Sir James Dewar. The practical application of the knowledge of these phenomena is well brought out in the concluding paragraph of this paper, where it states that if the glass upon which the condensation is to take place is covered beforehand with a thin film of some salt, no coherent

metal film is formed. This knowledge has already been applied by the makers of metal filament electric lamps to prevent the darkening that takes place by use, and it is stated that the insides of the glass globes have already been coated with very thin films of certain salts, and that the results have been very good indeed.

The formation of colloids by the electric pulverisation of metals is exhaustively discussed and a great number of illustrations of apparatus and particulars are given. At the end of this portion of the book is a very complete bibliography of work that has been done on the subject.

The latter part of the book is devoted to a treatise upon the formation of dispersed systems in liquids and in solids This chapter is full of the most interesting material. Chemical reactions, gold sols, Faraday's experiments, silver sols, silver mirrors, experiments of early investigators, the preparation of ruby glass, and kindred subjects are touched upon, ending with bibliography. The book concludes with a name and subject matter index.

We shall look forward with very great interest to the succeeding numbers of this valuable series of monographs.

*Priestley in America*, 1794—1804. By EDGAR F. SMITH, University of Pennsylvania. Philadelphia: P. Blakiston's Son & Co. Price $1.50.

The author has collected together a fund of interesting notes connected with the emigration of Priestley to America, his reception in that country, and the work he did during the period between 1794 and 1804. The value of the presence of Priestley seems to have been very fully recognised by the chemists of that country and his teaching had undoubtedly a great effect on the development of chemistry in the young Republic. The author has collected a great deal of matter from contemporary newspapers, documents, and books, and has endeavoured to weave the whole into a connected sketch. A great number of Priestley's original letters are reproduced, which are of deep interest not only to the American reader, but to chemists in general.

Priestley's fame as a chemist and also as a preacher appears to have been very greatly appreciated at the time. Some of the newspaper clippings show what that strange power, the newspaper world in those early days, thought of the Rev. Dr. Joseph Priestley. An account was given of a meeting at Columbian Tavern on March 27, 1797, in commemoration of his birth, where it is recorded that a number of toasts were given, from which we reproduce the following:

"That illustrious Christian philosopher, Joseph Priestley. May the world be grateful to him for his services, as his services are beneficial to the world.'"

"Truth—may the splendour of her charms dissipate the gloom of superstition and expel hypocrisy from the heart of man."

"White-robed Charity—may she accompany us in all our steps and cover us with a mantle of love."

The writer concludes that it was "a feast of reason. The purest philanthropy dignified the conversation, and moderation and temperance bounded every effusion of the heart."

Although strong appeals were made by Priestley's friends that he should return to England, he determined to remain in the land of his exile. He continued working to the end, and it is reported that he was in the very act of correcting the proofs of one of his papers when he died on February 6, 1804.

Those who realise the work that Priestley did in those early days of chemistry will undoubtedly take pleasure in the many instances recorded of the whole-hearted and simple manner in which he worked.

*Philosophy and the New Physics: An Essay on the Relativity Theory and the Theory of Quanta.* By LOUIS ROUGIER. Authorised translation from the author's corrected text of "La materialisation de l'Energie," by MORTON MASIUS, M.A., Ph.D. Philadelphia: P. Blakiston's Son & Co. Price $1.75.

The author in his preface suggests that physicists as a rule are occupied too much with their special field to give much attention to matters of more general philosophical interest, and few philosophers possess the knowledge of science required for discussing and criticising fruitfully the work of the physicist, and he states that the book marks a measurable advance toward a confluence of the broad streams of philosophical and scientific enquiry.

The first chapter is devoted to the dualism of matter and energy, and after a brief introduction deals with the difficulties of the dualistic theory and concludes with a chapter on the inefficiency of Ostwald's energetice and the experimental discovery of the inertia of energy. Some chapters are devoted to electro-magnetic dynamics and the weight and structure of energy, and the author discourses on the dematerialisation of matter and the materialisation of energy.

In a chapter on radio-activity and atomic degradation of the elements, there is an interesting account of the discovery of radio-activity that is of very great value on account of the brevity and great accuracy with which it is given.

It is stated that the glass walls of a Crookes' tube were found to emit X-rays, and soon after this discovery M. Poincare suggested that inasmuch as the phenomena of emission and phosphorescence are inter-related, a phosphorescent substance should emit X-rays. This led to the discovery by M. Becquerel of the radio-activity of the salts of uranium and finally to the discovery by Madame Curle of the elementary substance radium.

The book, although small, is of very considerable interest at the present time, and the bibliography at the end adds much to its usefulness.

*Introduction to General Chemistry: An Exposition of the Principles of Modern Chemistry.* By H. COPAUX. Translated by HENRY LEFFMANN, A.M., M.D. With 30 illustrations. Philadelphia: P. Blakiston's Son & Co. Price $2.

The translator has done a real service to chemists by producing Prof. Copaux's work in English, and its value is greatly enhanced by the fact that Prof. Copaux was in touch with the translator while the work was in progress and suggested some changes in phraseology that add

to the lucidity of the text.

The book opens with an introduction giving the idea of the elements and the law of the conservation of matter. The atomic theory, chemical formulæ, inter-relation of the elements, properties and theories of solutions in chemical affinity are dealt with. A very good chapter is devoted to the atomic weights of the radio-active elements and Moseley's table of atomic numbers is discussed.

A large number of diagrams are given and an appendix at the end of the book deals with the structure of crystals and a contribution by the translator on hydrogen ion concentration.

## CORRESPONDENCE.

### BLINDED SOLDIERS' & SAILORS' HOSTEL.

*To the Editor of the Chemical News.*

SIR,—At this moment of my own and my mother's deep personal loss, I feel sure that I am voicing what would have been my father's wishes in asking that the public who have so fully and generously supported his unceasing work for St. Dunstan's and the National Institute for the Blind, should continue to help that work in every possible way.

My father's deepest concern was that the public should regard his work for the blind not merely as a personal effort of his own, but as a National Trusteeship placed in his hands by the people of the Empire.

I ask, therefore, in his name, that all present and projected activities to raise the much-needed funds for the work to which my father devoted his life should continue without ceasing for a moment. I am sure that he would have wished this.—I am, &c.,

NEVILLE A. PEARSON.

Headquarters of St. Dunstan's Work,
Inner Circle, Regent's Park, N.W.1.

### ENGLISH IN LATVIA.

*To the Editor of the Chemical News.*

SIR,—The British public will be interested to hear that Latvia, one of the new Baltic States, has decided to make English the first foreign language to be taught in its University and schools. English and English ideals will, therefore, henceforth take a very important place in the education of this new State, with which our country has very close and other relations.

But the teaching of English is sadly hindered by the dearth of good books in our language, and the purchase of these at the present time by the Letts is impossible owing to the very adverse rate of exchange. The want which this condition of things reveals is one, however, which could easily be supplied, at very little cost to itself, by the British public, which now has a great opportunity to befriend a nation which has suffered much through the war and which earnestly desires to draw closer the ties of its friendship with Great Britain. There must be scores, nay hundreds, of thousands of books—standard works in our language, disused school books, useful in the teaching of English, as also scientific, engineering, and other professional works—for which their owners no longer have any use. It is for gifts of such books, as well as any others which can be spared, that I now appeal

My appeal has the support of the following: Prof. Gilbert Murray, Sir Richard Gregory, Brig.-General A. Burt (late British Military Commissioner to the Baltic States), Mr. G. S. Tallents, C.B. (late British Commissioner in Latvia), Dr. Hagberg Wright (Hon. Secretary, Friends of Latvia), Mr. J. F. Green, M.P., and Mr. H. C. Woolmer. At their invitation Sir Alfred Davies, who so successfully organised the supply of educational books to our British and Colonial prisoners during the war, has kindly consented to direct the arrangements for book collections, and his former coadjutor, Mr. H. W. Atkinson, M.B.E., will give his services as Hon. Librarian.

May I, therefore, ask all who can spare, from their shelves, English books will, without delay, forward them to Sir Alfred T Davies, K.B.E., C.B., c/o The Consul-General for Latvia, 329, High Holborn, London, W.C.1. I should like to be in a position, on behalf of the citizens of this country, to make a New Year gift to Latvia of at least 50,000 volumes.—I am, &c.,

JOHN BADDELEY,
*Lord Mayor of London.*

Mansion House,
December 3, 1921.

## BOOKS RECEIVED.

"Laboratory Exercises in Applied Chemistry for Students in Technical Schools and Universities." By Dr. WILHELM MOLDENHAUER. Authorised translation by LAWRENCE BRADSHAW, D.Sc., Ph.D. Pp. vi.+236, with 36 Illustrations. 1921. London: Constable & Co. Price 12s. 6d.

"Elementary Chemical Microscopy." By EMILE MONNIN CHAMOT, B.S., Ph.D. Second Edition, partly rewritten and enlarged. Pp. xv.+476. New York: John Wiley & Sons Price 25s.

"Rays of Positive Electricity and their Application to Chemical Analysis." By SIR J. J. THOMSON, O.M., F.R.S. Second Edition, with Illustrations. Pp. x.+237. London: Longmans, Green & Co. Price 16s.

"Chemical Reactions and their Equations: A Guide and Reference Book for Students of Chemistry." By INGO W. D. HACKH, Ph.C., A.B. Pp. viii.+138. Philadelphia: P. Blakiston's Son & Co. Price \$1.75.

"The Manufacture and Uses of Explosives." By R. C. FARMER, with Foreword by SIR ROBERT ROBERTSON, K.B.E., F.R.S. Pp. viii.+116. London: Sir Isaac Pitman & Sons, Ltd. Price 2s. 6d

"Oils, Fats, and Fuels." By THOMAS HULL. Pp. viii.+143. 1921. London: Blackie & Sons; Glasgow and Bombay. Price 3s. 6d.

"Introduction to General Chemistry: An Exposition of the Principles of Modern Chemistry." By H. COPAUX. Translated by HENRY

LEFFMANN, M.A., M.D. Pp. x.+195, with 30 illustrations. Philadelphia: P. Blakiston's Son & Co. Price $2.

"Philosophy and the New Physics: an Essay on Relativity and the Theory of Quanta." By LOUIS ROUGIER. Authorised translation by MORTON MASIUS, M.A., Ph.D Pp. xv.+159. Philadelphia: P. Blackiston's Son & Co. Price $1.75.

"Priestley in America, 1794—1804." By EDGAR F. SMITH. Pp. 173. Philadelphia: P. Blakiston's Son & Co. Price $1.50.

"Fuel and Lubricating Oils for Diesel Engines." By W. SCHENKER. Pp. xii.+112. London: Constable & Co. Price 10s. net.

"Year-Book of Pharmacy—comprising Abstracts of Papers relating to Pharmacy, Materia Medica, and Chemistry." With Translations of the British Pharmaceutical Conference. Pp. 418. London: J. & A. Churchill.

"A Text-book of Inorganic Chemistry." By A. F. HOLLEMAN, Ph.D., F.R.A. (Amst.). Issued in English in co-operation with HERMON CHARLES COOPER. Sixth English Edition, revised. Pp. viii+527. London: Chapman Chapman & Hall, Ltd. New York: John Wiley & Sons. Price 9s

"The Emission of Electricity from Hot Bodies" By O. W. RICHARDSON, F.R.S. Second Edition. Pp. viii.+320. London: Longmans, Green & Co. Price 16s.

## NOTES.

THE Library of the Chemical Society will be closed for the Christmas holidays at 1 p.m. on Friday, December 23, and will reopen at 10 a.m. on Thursday, December 29.

ROYAL INSTITUTION.—The following are the lecture arrangements at the Royal Institution before Easter. Prof. J. A. Fleming—six lectures adapted to a juvenile auditory on "Electric Waves and Wireless Telephony," beginning on Thursday, December 29, on "Surface Waves on Liquids," followed by "Waves in Air," "The Telephone," "Electric Oscillations," "Electric Waves," and "Wireless Telephony." On Tuesday afternoons, commencing on January 17, there will be two lectures on "Physiology as Applied to Agriculture" by Dr. F. H. A. Marshall, three by Prof. H. H. Turner on "Variable Stars," five by Sir Arthur Keith on "Anthropological Problems of the British Empire," Series I., Racial Problems in Asia and Australasia," and two by Dr. J. W. Evans on "Earth Movements." On Thursday afternoons Mr. Seton Gordon will give two lectures on "Mountain Birds of Scotland and Sea Birds and Seals," Sir Napier Shaw two on "Droughts and Floods," Prof. A. G. Perkin two on "Dyeing: Ancient and Modern," Prof. H. Maxwell Lefroy two on the "Menace of the Insect Pest: The Balance of Life in Relation to Insect Pest Control," Dr. P. Chalmers Mitchell two on "The Cinema as a Zoological Method," and Prof. A. Hind two on "Landscape Etchers: New and Old." On Saturdays there will be two lectures by Dr. L. de Selincourt on "Humourists of the Seventeenth Century," (1) "Sir Thomas Browne," (2) "Thomas Fuller"; two by Prof. E. A. Gardner on "Masterpieces of Greek Sculpture," and six by Sir Ernest Rutherford on "Radioactivity." The first Friday Evening Discourse will be given on January 20 by Sir James Dewar on "Soap Films and Molecular Forces." Succeeding Discourses will probably be given by Viscount Burnham, Sir Francis Younghusband, Prof. D. Halliburton, Dr. R. S. Watson, Prof. J. Joly, Dr. C. M. Wenyon, Prof. T. R. Merton, Dr. A. P. Laurie, Prof. F. G. Donnan, Mr. A. B. Walkley, Sir Ernest Rutherford, and other gentlemen.

MANCHESTER LITERARY AND PHILOSOPHICAL SOCIETY (Chemical Section).—Dr. H. F. Coward, F.I.C., has been elected Chairman of the Section for the Session 1921-22. At the meeting of the Society held on Tuesday, November 29, Prof. Horace Lamb, M.A., Sc.D., F.R.S., Sir Ernest Rutherford, M.A., DSc., F.R.S., Sir Arthur Schuster, Ph.D., Sc.D., F.R.S., F.R.A.S., and Prof. G. Elliott Smith, M.A., M.D., F.R.S., were elected Honorary Members.

THE *Journal of the Society of Leather Trades Chemists* for November, 1921, contains an interesting paper upon the action of formaldehyde upon gelatin. The fact that gelatin is rendered insoluble by formaldehyde is considered to have been first brought into prominence by Ernest O. Beckmann in 1894. The paper contains a deal of interesting information, and the interest in this reaction for those engaged in leather technology is dealt upon. Formalin-gelatin is practically insoluble in cold water, and only slightly soluble in hot water. A long-continued heating in water results in the complete expulsion of formaldehyde and reversion to gelatin of the ordinary type. The elasticity of a gelatin-gel decreases enormously as it absorbs formaldehyde. The product has almost the brittleness of glass, and when broken it shows a conchoidal fracture. Sudden heating causes it to crack like glass under analogous conditions. This seems to point to a condition of strain and it led to an optical examination. The result was negative, and the conclusion was that formalin-gel is not under any physical strain corresponding to such strain as exists in glass.

DENMARK.—The Danish State Railways invite tenders for the supply of various pigments, soaps, and heavy chemicals. The specification enumerates the following articles (the tons are metric tons): 2 tons of dry lead white in lumps, 4 tons red lead, 1½ tons of zinc white, 3 tons of lamp black, 1½ tons of chestnut brown, 1 ton of light umber, 1·6 tons French yellow ochre, 80 tons crystal soda, 10 tons of extra fine whiting, 2 tons polishing powder, 47 tons of soft green or brown soap, and 3 smaller items of soaps, 2·2 tons of denatured spirits of wine for varnish and polish manufacture, 4 tons of turpentine oil (either French or mineral), 550 kgs. of nitric acid, 32 tons of 27 per cent sulphuric acid for use in accumulators, and 2½ tons of ammonia (S.G. ·963-·955). Tenders are to be in the hands of the "Maskinafdelingens Kontor," Trommesalen 5, 3rd Floor, Copenhagen, B., by 1 p.m. on Dec. 29. A copy of the specification and conditions of tender forwarded by the Commercial Secretary to H.M. Legation in Copenhagen (in Danish) can be seen by United Kingdom firms interested on application to the Department of Overseas Trade (Room 84), 35, Old Queen Street, Westminster,

S.W.1. A copy is also available for firms in the provinces unable to arrange for its inspection in London.

CONGO.—Notwithstanding the commercial depression in the Congo, satisfactory business is being obtained by some travellers to that country, and if the traveller is unsuccessful the reason is often to be found in his own unsuitability for dealing in that market. Such is the conclusion to be drawn from a dispatch on this subject from the Acting British Consul at Boma, who finds it necessary to remind United Kingdom firms of the difficulties to be encountered by their travellers if the latter speak the English language only, or are not fully prepared to quote prices French is essential, and Portuguese desirable. The Consul is prepared to give advice and full information concerning the merchants in his district to United Kingdom commercial travellers who, he hopes, will not fail to call at the Consulate and make use of the assistance he can give.

THE "ABDULLA" 1922 ALMANACK.—An "Abdulla" Almanack for 1922 has been published by the Bond St. cigarette specialists of that name. In accordance with the usual annual practice of the firm, 10,000 copies are offered for sale, at the price of 1s. 6d. for the benefit of the British Red Cross Society, Abdulla & Co. bearing the expenses of production. As the Almanack contains twelve coloured illustrations, each specially drawn for the publication by a leading artist, there should be no difficulty in selling all the copies, and the maximum benefit to the Red Cross Society should be assured. We have seen a copy of this Almanck. Apart from its philanthropic purpose which is greatly to be commended, it is a splendid production far beyond the usual illustrated almanack, and Messrs. Abdulla are not only doing patriotic service in helping the Red Cross Society, but have given us something that will be a pleasure to see during the coming year. The printing is by the Spencer Press, Ltd., who are to be congratulated upon the work.

## New Patents

THIS List is specially compiled for the *Chemical News* by Messrs Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W C.2., from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

31055—Dutt, E. E.—Process for manufacture and extraction of titanium dioxide and vanadiumoxide from bauxite ores. November 21

31085—Meter, J.—Method for diffusing and disseminating poisonous gases. November 21

31087—Moritz, R.—Stirring-device for mechanically-operated sulphate furnaces. November 22

31241—Moritz, R.—Apparatus for measuring acids, etc. November 22

31276—Roka, K.—Chlorination of methane. November 22

*Specifications published this Week.*

147118—Grunstein, N.—Manufacture of butyric aldehyde and butyl alcohol from crotonic aldehyde

149662—Verine Chemischer Fabriken in Mannheim.—Manufacture of sulphur dioxide by heating sulphates of alkaline earths, magnesium, and iron

171149—Mooney, F. M—Manufacture of a solution of chromic sulphate

171281—Howards & Sons.—Manufacture of calcium magnesium and lithium acetylsalicylates

71292—Fohnson, J. Y.—Manufacture and production of anthraquinone derivatives

*Abstract Published this Week*

*Dyes, Lakes.*—Patent No. 170155—A new compound and process for obtaining Monoazo dyes, has been invented and Patened by F. Bayer & Co., of Leverkusen, near Cologne, Germany. Soluble chromium compounds of the monoazo dyes from diazotized anthranilic acid or its derivatives not containing hydroxyl groups and B-napthylamine sulphonic acids, or of those from diazotized anthranilic sulphonic acids and B-napththylamine, are obtained by boiling the dyes with chromium compounds In an example, diazotized anthranilic acid is coupled with 2-napthlamine-7-sulphonic acid, the dyestuff salted out, boiled with chromium fluoride and water, and the chromium compound salted out; the anthranilic acid may be replaced by its chlor—and nitro-derivartives such as $C_6H_3(COOH).(NH)_2:Cl = 1.2:4$, $C_6H_3(COOH)(NH_2)\cdot(NO_2) = 1:2:5$ or $1:2:4$; and the 2:7-napthylamine sulphonic acid can be replaced by 2-napthylamine di- or tri-sulphonic acids; further sulpho anthranilic acids such as $C_6H_3(COOH).(NH_2):(SO_3H) = 1.2:5$ or $1.2.4$ can be coupled with 2-napthylamine.

*Lakes.*—Barium, calcium, and aluminlum lakes can be prepared from the above-described chromium compounds; the compound of the example yields pure reddish-violet lakes fast to water, lime and light.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

# NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemica Apparatus, &c., for review or notice to be addressed to the EDITOR.

**SUBSCRIPTIONS,** £1 12s. per annum, payable in advance should be addressed to the MANAGER.

**BACK NUMBERS and VOLUMES** can be purchased on application to he MANAGER

THE CHEMICAL NEWS,
97, SHOE LANE, LONDON, E.C.4

## ADVERTISEMENTS.

**All communications for this Department should be addressed to—**

T. G. SCOTT & SON,
63, LUDGATE HILL, LONDON, E C.4.

THE CHEMICAL·NEWS.

VOL. CXXIII, No. 3219.

## LINE ENTITIES AND LINE DOMAINS

### PART I.

By F. H. LORING.

THE physical and chemical worlds, if a distinction thus be made, cannot be built up entirely of atomic entities—electricity, in the electronic sense, included. Nor can the atomic world be constructed without something beyond the nuclear part of the atom. This *something* may be summed up by the term *atomic domain*.

Magnetism and static electricity are best comprehended by the scheme of lines of force. The atomic structures are known to be electric in character. Radio-activity reveals clearly the electrical architecture. Thus there are *atomic nuclei, atomic domains* and *lines of force*.

Everyone who has given these matters thought must have wondered whether the lines of force are not themselves incomplete without some sort of domain—a kind of line domain. It is true that one speaks of a *tube* of force, but this does not exactly involve the domain idea as derived by analogy from the atom. These atomic domains seem to restrict the interpenetration of those atoms adjacent to each other (see W. H. Bragg's paper in the *Phil. Mag.*, 1920, xl., 169).

Passing now to the problem of radiation, there is a lack of continuity observed when studying the behaviour of radiant energy and Planck's universal quantum constant known as $h$ has become an important factor in formulating radiation phenomena; that is to say, it is expressed in bundles of $h$, so to speak, to agree with experiment. Radiation is not, however, strictly speaking, a process that can be truly described as atomic. It seems to identify itself with lines of force, since Hertz waves are nothing other in principle than light waves of great length, in which case lines of force are in marked evidence when considering the electrical aspect of the phenomenon.

A serious difficulty arises in this case; for if light is essentially tremors transmitted along definite lines of force, one has only to examine the wave-front some distance from the light source to expect to find proof of points of light widely spaced. No such effect has been found, although experiments have been made with the object of detecting such separated quanta or such spaced lines in vibration, assuming the line-undulation idea to constitute radiation (see in this connection CHEMICAL NEWS, 1920, cxx., particular pages 195 and 196).

It is true that the Hertz waves are not necessarily interpreted exactly in this way, for the orthodox conception of lines of force coming into existence and disappearing again involves magnetically the lines springing from a point and expanding into larger and larger circles, then contracting into smaller and smaller circles until they cease to exist; but this may be a sort of resultant effect, as if the lines already existed in space in a neutralised state, and when a wave is started this neutralisation is destroyed and it passes out as if it were an expanding line circle of force, whereas the radial line may simply convey the wave (see CHEMICAL NEWS, 1917, cxvi., 181).

Returning to the atomic domain conception, this seems to be in harmony with Bohr's theory of the hydrogen atom, in which circumstance the domain-size of the atom is defined by the radius of the electron orbit, and under conditions of great freedom a very large atom should result. It will be remembered, moreover, that according to the views advanced by Langmuir, in developing the octet theory, "the large atomic volumes of the alkali metals are due to the volumes occupied by single free electrons rather than to a large volume of the atom as such."

It is, of course, the movement of the electron in the atom which is supposed to give rise to radiation, and according to Bohr's theory this takes place when the electron passes from an orbit of radius A to one of less radius, B the energy given out as radiation being in multiples of $h$, Planck's constant $6{\cdot}55 \times 10^{-27}$ erg×second, so that $A—B = h\nu$, $\nu$ being the frequency of the radiation. In this case the positive nucleus of the atom is the sun, as it were, to the planetary system having one planet, the electron, in the example of the hydrogen atom. Sommerfeld has accounted for the fine-line structure of the hydrogen series lines by assuming that the electron describes elliptical orbits, as owing to its increase in velocity at the times when it passes closer to the nucleus it suffers a change in mass according to the theory of relativity. At any rate, the positive nucleus of practically point magnitude (according to Rutherford) serves to anchor the electron.

In a similar way, that is to say, by analogy, the extended line of force may serve to anchor the domain exterior to it—assuming such a domain. If now this domain partakes of the vibration of the line and the expanding wave-front involves expanding unit-domains, then there need be no discontinuity as would be the case if there was no line domain. Such a line domain taken as a single unit would be a cone formed round an axial line of force.

So far, so good; but problems arise. It is difficult to conceive all space filled with such lines and their domains. Moreover, it would be expected that such a complex of lines and their domains would in some way be linked up with gravitational fields existing round bodies (see CHEMICAL NEWS, 1917, cxvi., 181). It is at this point that the mathematician has the advantage over those who adhere rather closely to models; for the former can proceed to evaluate quantities and formulate their action or interaction along such lines as agree with experimental results. He may not be able to picture what his equations represent in terms of mechanism, but he may nevertheless deduce laws agreeing with experiment. The theory of relativity in its extended form assigns to space peculiarities usually associated with matter; or the geometry of space becomes endowed with physical properties. This has proved to be a great help in the solution of difficult problems. As an example, the following from a recent article of mine will serve as an illustration. "Passing over considerable ground and turning to the culminating achievement of the

theory in its more extended form . . . the bending (or drawing-in, in the sense that converging railway lines would bring the trains closer together) of the course of light in passing close to the sun, owing to the concentration of the space-gravitational field (by analogy, the railway-lines) round this massive body (due to the mass-energy of the sun, as it might be termed), was clearly foreshadowed quantitatively by a development of the theory, and the phenomenon was verified by the photographs taken at the last eclipse expedition (see CHEMICAL NEWS, 1920, cxxi., 277)".
(see CHEMICAL NEWS, 1920, cxxi., 277)". The fact that all bodies fall with the same acceleration in a vacuum fits in perfectly with the idea of a field, just as a light shunting engine would follow the same track-course as a heavy goods-train locomotive, in the foregoing analogy; but examples of this kind cannot be pressed to extremes.

If now the principle underlying relativity be grasped, it will be seen that the line domain idea can be treated possibly in a similar manner, and as a result, the complexity referred to above may not involve such a hopeless maze of unresolvable entities as to resist mathematical analysis

It will, therefore, be desirable to review briefly the main features of relativity. In the first place, the interaction of attracting bodies and their relative movements as developed by Newton, involve by analysis the conception of a fixed background of space and time, and so far as the movements of bodies in what might be termed a self-contained system* are concerned, no difficulty arises, but problems arose in which the self-contained idea in the wide sense became inoperative; that is to say, movements were known which did not agree with the older theory. This fact brought into prominence the principle known to mathematicians: that complex phenomena can be resolved into working components each one of which obeys an invariant law under the conditions specified, and when dealing with such phenomena it became necessary to define what is really meant by relative effects or relative motions. In this newer idea it became necessary to treat all observed phenomena as *appearing* differently to different observers if they were in relative movement with respect to one another; or simplifying matters by considering *two* bodies or systems in relative movement implying observers attached to each system, the words *each other* would be substituted for *one another*. In short, each system in movement had attached to it its own Euclidean -space framework of three dimensions. When two such frames of reference were in relative movement with respect to each other, it became necessary to define the *observer's* view. To do this, it became also necessary to show how the two systems could be related to each other so that each observer could determine consistently the peculiarities of the system he was observing—the one, say, in relative movement with respect to his own. This was accomplished by making use of what is known as the Lorentz transformation equations. These equations are justified, for, by their use answers agreeing with experiment were obtained.

* This term is used in a restricted sense, as when experiments are carried out, for example, on a railway train under uniform straight-line movement. To one stationed on the ground a difficulty would arise owing to the relative movement. This has been thoroughly described in relativity books and it need not be detailed here.

The question of *reality* arises when phenomena are taken as within themselves individually invariant, but relatively variant to each other Events which are simultaneous to an observer in may not be simultaneous to another observer in movement with respect to the event being observed. Hitherto the phenomenon was the real thing and all observational formulisation of it the imaginary (image) part. Now the real invariant thing is the law or its formulisation and the imaginary (appearance) part is the phenomenon as observed; but the real part is the small point-time event: the "element" taken complete enough to represent or correspond to the law involved.

It will be seen that by this method the idea of each phenomena (perhaps one should say *its aspect*) when resolved had its own law and in a sense pursued an independent course quite apart from some other phenomenon, which ordinarily would be considered as a part and parcel of it. Differential or conjoint results do, however, arise due to the observer's point of view, but the phenomenon itself is quite independent by analysis, in that it, in common with the neighbouring one, obeys accurately a common law. Dalton's law of partial pressures will serve here as an example "This law states that the pressure due to a mixture of gases is equal to the sum of the pressures exerted by each gas singly when confined in the same space as that containing the mixture" to quote from my "Atomic Theories" (Methuen) p. 5. Here is a case of the interaction of mixed gases without altering the pressure values as obtained by considering each quantity of gas singly, *i.e.*, as if only one gas existed when evaluating its contribution to the total pressure.

Two other examples might be given here. An electrostatic field is an electrostatic field to a stationary observer; but to a relatively moving observer it becomes an electromagnetic field. Here is one fundamental phenomenon having two aspects; or in terms of invariant law each aspect represents the invariant law, which by relative and non-relative movement becomes respectively magnetic and static fields. Gravity and inertia are similarly connected; each is a fundamental "invariant," but according to circumstance the results differ In one extreme centrifugal force is apparent, in the other, the "apple falling to the earth." One is an inertial effect, the other is a gravitational effect, but these become circumstantial variations of the same fundamental phenomenon. Inertial mass and gravitational mass thus become fundamentally identical.

Now before leaving the relativity method of analysing effects or phenomena, it will be desirable to mention that the three space co-ordinates attached to each system in movement imply also time; but the time so implied is in effect the displacement of one such system with reference to the other; and along with this displacement the idea of space being associated with time (or this time) becomes evident. Or, looking at it in another way, each system has its own time and space, time becoming a fourth dimension in the system.† Moreover, the velocity of light becomes the basic factor in harmonising space and time. In the relativity equations the measurements are

† "The fundamental measurement is not the interval between two points of space, but between two points of space associated with instants of time."—Eddington.

all made with a *constant* appearing in the calculation, which is the velocity of light in a vacuum or space free from matter. Why this particular velocity? This question was raised by Sir Oliver Lodge (see *Nature*, 1921, cvii., 716, 748). For instance, what has the velocity of light to do with the increased mass of the planet Mercury when it sweeps round the sun at its closest approach to this body; *i.e.*, when it moves fastest? We know that by introducing the relativity equations and calculating the increased mass the orbit would be slightly expanded at the perihelion, and, as a consequence, in one hundred years the orbit will have advanced, or rather, turned through an angle of 43 seconds, after allowance has been made for the perturbing effect of the other planets during the century interval.

Here is a purely mechanical problem, apparently, yet the velocity of light is an electromagnetic movement. The answer is that all our mechanics when fundamentally analysed in the ultimate sense involve electrical phenomena, or conversely, all electrical phenomena properly analysed are resolvable into mechanical effects, but the mechanics is the mechanics of Einstein.

Not only do we construct all the elements' atoms out of positive and negative electrons, but we extend their fundamental characteristics to space itself, so that radiation becomes a sort of counterpart to the atomic system, only drawn out linearly and expanded spacially instead of functioning in a circulatory manner.

This brings one now to the line-domain conception, for here in a sense is an actual framework, as it were, extending from points, from atoms say, and this somewhat resembles the fourth dimension figure given in the CHEMICAL NEWS, 1921, cxxiii., 218. Treated in a relativity sense, this becomes a physical frame of reference attached to each moving body—to each atom or atom part—so that space is curved in the Einstein sense if equipotential planes (curved surfaces) are taken across the line domains (see CHEMICAL NEWS, 1917, cxvi., 181). In other words, the curvature of space and the gravitational field therein (see quotation above briefly describing the bending of light) seems compatible with the idea of expanding line domains (see CHEMICAL NEWS, 1915, cxii., particular page 100) so that in effect the lines of force are not of uniform section; and, that which is here considered an important feature, the continuity of the wave-front, follows apparently as a natural consequence.

Considering now the photo-electric effect, the question might be raised: Can such line domains re-concentrate on electrons and account for the photo-electric effect which seems to require more energy than can be obtained from a point in space?

It is well to bear in mind that the discussion of ideas in the foregoing manner involves one in philosophical subleties, but I venture to suggest that the idea of line entities and line domains are not without suggestive interest.

*Summary.*

By analogy with atomic domains, involving forces which are best expressed as electric line fields, there may be line domains. Such line domains considered from the point of view of relativity seem to follow as a necessary consequence and radiation would thus be rendered continuous at the wave-front. The question is raised as to whether such line domains can re-concentrate on electrons and thereby account for the energy necessary to produce the photo-electric effect? It is felt that philosophical difficulties exist in speculations of this kind, but the ideas in question seem suggestive.

## THE ELECTROLYSIS OF AQUEOUS SOLUTIONS OF ALKALINE NITRITES WITH A LEAD ANODE AND AN ELECTRO-METRIC DETERMINATION OF THE CONSTITUTION OF THE COMPLEX ANION FORMED *

By F. H. JEFFERY, M.A., Trinity College, Cambridge.

THE experiments described in this paper form part of a series of experiments which deal with the passage of electricity during electrolysis from various metallic anodes to aqueous solutions of sodium nitrite.

Reactions which take place with a silver anode and with a copper anode have been described already.

Silver goes into solution entirely as complex anion $(Ag(NO_2)_2)'$ crystals of $Na(Ag(No_2)_2).\frac{1}{2}H_2O$ can be be isolated from the anolyte (*Faraday Soc. Trans.*, 1920, xv., 16).

Copper also goes into solution entirely as complex anion, this anion is $(Cu(No_2)_6)^{iv}$ derived from divalent copper; $K_2Pb(Cu(NO_2)_6$ can be isolated from the anolyte and from this $K_4(Cu(NO_2)_6).2H_2O$ can be prepared (*Ibid.*, 1921, xvi., 453).

The following is a description of that which happens when the anode is of lead:—

*Arrangement of Apparatus for Electrolysis.*

The cell was a glass dish inside which was a porous pot containing the cathode of smooth platinum, this latter was placed so as not to touch the bottom of the pot. The anode was of area 50×2 cms.², it was bent into a cylindrical shape so as to stand on the bottom of the glass dish, a glass stirrer turned by a motor revolved rapidly close to it. The dish and its contents were placed in a large vessel of water, thereby maintaining the temperature of the anolyte at 17° to 18°.

When the electrolysis had to continue for many hours, it was necessary to suppress the migration of hydroxidion through the cathode pot to the anolyte. This was done by placing the cathode pot inside another porous pot of about double its diameter, the space between the two pots being filled with an anolyte solution which had been obtained from previous electrolysis. Outside this larger pot was the anolyte which was being investigated.

The sodium nitrite used was free from chloride and contained 99·0 per cent pure $NaNO_2$, the rest being sodium nitrate.

The anolyte solutions were of various concentrations from 6·9 grms. sodium nitrate per 100 grms. water to 27·6 grms. sodium nitrite per 100 grms. water. The volume of the anolyte was 200 cc.

* Read before The Faraday Society, November 28, 1921.

The currents varied from 0·099 amps. to 0·77 amps.

Pure lead was used for the anode; Col. C. T. Heycock most kindly gave many hundred grms. of the metal from a stock of pure material which he had prepared for his own use.

The liquid in the cathode pot was a solution of sodium nitrite of the same concentration as that used for the anolyte.

*General Effects.*

For variations of current and of concentration of sodium nitrite within the limits stated, lead was never deposited on the cathode, although some of the electrolyses continued during more than 24 hours.

The lead went into solution at the anode, forming a complex which gave a bright orange colour to the anolyte This latter was not at any time acid to indicators, nor was any gas evolved at the anode.

The complex lead anion was derived from divalent lead; sodium hydroxide added ot the anolyte gave a white precipitate soluble in excess; when hydrogen peroxide was added and then sodium hydroxide a chocolate precipitate of lead peroxide was formed. A solution of sodium sulphate gave a precipitate of lead sulphate.

A solid formed at the anode and adhered to it, but the electrical resistance of the cell was not affected appreciably thereby. This solid consisted of lead nitrite mixed with finely divided lead, the latter could be isolated easily by means of very dilute acetic acid.

*Apparatus for Measuring the Anode Potential during Electrolysis.*

For these measurements a cadium cell and a potentiometer of the "Granta" type by Messrs. Pye were used. The normal electrode was Ag | AgCl, nKCl |, the diffusion potential was suppressed by concentrated ammonium nitrate solution, the syphon tube connecting this solution with the anolyte being filled with sodium nitrite solution of the same concentration as that used for the anolyte.

Two normal electrodes were used, each dipping into the same ammonium nitrate solution, one of these was kept as a standard with which to compare the other, which was used for the electromotive force measurements.

The anolyte was stirred continuously during all measurements.

Pure sodium nitrite free from nitrate was used for the anolyte and for filling both the porous pots.

The normal electrodes, ammonium nitrate vessel and electrolytic cell were placed in a thermostat containing 92 litres of water This was heated by gas, delivered at constant pressure from a regulator. The regulation of the temperature was effected by the expansion of alcohol contained in a lead pipe 14ft. long and ⅜in diameter, which was bent into a helix, reaching from the bottom of the water to within about 9 cms. of the top. The water was stirred vigorously.

By these means the temperature was maintained at 18° ±0·003°.

*The Anode Potential during Electrolysis.*

The electromotive force of the combination was taken with the current on and then immediately after the current was off; after each pair of measurements the lead anode was washed with dilute nitric acid and with water and dried.

The lead anode was the negative pole of the combination.

(i.) An anolyte four times weight normal with respect to sodium nitrite containing 1·39 grm. of lead per 100 cc. of the solution :—

| Current in Amps. | E.M.F. in Volts, Current on Ag+to Pb. | E.M.F. in Volts, Current off, Ag+to Pb. |
|---|---|---|
| 0·099 | 0·5451 | 0·5481 |
| 0·19 | 0·5451 | 0·5481 |
| 0·29 | 0·5426 | 0·5471 |
| 0·38 | 0·5431 | 0·5471 |
| 0·48 | 0·5451 | 0·5481 |
| 0·58 | 0·5451 | 0·5481 |
| 0·67 | 0·5421 | 0·5481 |
| 0·77 | 0·5411 | 0·5481 |

The mean value of E.M.F. current on was 0·544 volts.

The mean value of E.M F. current off was 0·548 volts.

Taking the potential of the normal electrode at 18° to be 0·5130 volts, the silver being positive to the solution, the following results were obtained :—

The mean value of anode potential current on −0·031 volts.

The mean value of anode potential current off −0·035 volts.

(ii.) An anolyte four times weight normal with respect to sodium nitrite containing 2·55 grms. of lead per 100 cc. of the solution :—

| Current in Amps. | E.M.F. in Volts, Current on, Ag+to Pb. | E.M F. in Volts, Current off, Ag+to Pb. |
|---|---|---|
| 0·099 | 0·5350 | 0·5375 |
| 0·19 | 0·5325 | 0·5375 |
| 0·29 | 0·5345 | 0·5375 |
| 0·38 | 0·5345 | 0·5375 |
| 0·48 | 0·5345 | 0·5375 |
| 0·58 | 0·5325 | 0·5375 |
| 0·67 | 0·5335 | 0·5375 |
| 0·77 | 0·5315 | 0·5365 |

The mean value of E.M.F. current on was 0·534 volts.

The mean value of E.M.F. current off was 0·538 volts.

These results gave :—

The mean value of anode potential current on −0·021 volts.

The mean value of anode potential current off −0·025 volts.

From these measurements it appears that the degree of dissociation of the complex lead anion must be very small under these conditions; for a wide range of current nitensity the concentration of plumbous ion remains constant and low, the rate of work involved in the transfer of electricity from anode to anolyte in contact with it being simply proportional to the current.

There is no evidence from these two series of measurements that more than one species of complex is formed.

*The Anode Potential during Electrolysis of Solutions containing both Nitrate and Nitrite.*

Two series of measurements at 18° were made with four times weight normal solutions of sodium nitrite to which sodium nitrate had been

added. The object was to find whether the anode potential would rise and the anode react with the $NO_3$ ions present forming plumbous ions in concentration sufficient to give a deposition of lead on the cathode.

(i.) An anolyte four times weight normal with respect to sodium nitrite containing 1·50 grms. of lead per 100 cc. of the solution, to which were added 8·7 grms. of sodium nitrate.

| Current in Amps. | E.M.F. in Volts, Current on, Ag+to Pb. | E.M.F. in Volts, Current off Ag+to Pb. |
|---|---|---|
| 0·099 | 0·5349 | 0·5399 |
| 0·19 | 0·5349 | 0·5389 |
| 0·29 | 0·5349 | 0·5399 |
| 0·38 | 0·5339 | 0·5399 |
| 0·48 | 0·5349 | 0·5399 |
| 0·58 | 0·5349 | 0·5399 |
| 0·67 | 0·5344 | 0·5399 |
| 0·77 | 0·5349 | 0·5399 |

These results show that the anode potential remained constant for the same range of current intensity as that used for nitrite alone, being −0·022 volts with the current on and −0·027 volts with the current off.

(ii) An anolyte four times weight normal with respect to sodium nitrite containing 2·95 grms. of lead per 000 cc. of the solution, to which were added 8·7 grms. of sodium nitrate.

| Current in Amps. | E.M.F. in Volts, Current on, Ag+to Pb. | E.M.F. in Volts, Current off, Ag−to Pb. |
|---|---|---|
| 0·099 | 0·5287 | 0·5307 |
| 0·19 | 0·5292 | 0·5312 |
| 0·29 | 0·5292 | 0·5312 |
| 0·38 | 0·5292 | 0·5312 |
| 0·48 | 0·5292 | 0·5312 |
| 0·58 | 0·5287 | 0·5312 |
| 0·67 | 0·5287 | 0·5312 |
| 0·77 | 0·5277 | 0·5307 |

These results are similar to those in (i.), the anode potential being −0·016 volts with the current on and −0·018 volts with the current off. The average rate of work involved in the transference of electricity from anode to anolyte in contact with it is of the same order as that in the two previous cases where no nitrate was present, it is likewise proportional to the current. The presence of the nitrate does not cause such an increase of the concentration of plumbous ion at any current intensity as to give a deposition of lead on the cathode.

### *Determination of the Constitution of the Complex Anion by Means of Potential Measurements.*

The electromotive force E volts of the combination Ag | AgCl, nKCl | conc solution $AmNO_3$ | anolyte | Pb was measured, the total concentration of lead [M] grm. atoms per litre of the anolyte solution was small. Representing the complex lead anion by $Pb_x(NO_2)_y$ and assuming that the law of mass action is applicable to the dissociation of the anion

$$[Pb_x(NO_2)_y] = K[Pb'']^x[NO_2']^y$$

also $E = c - 0{\cdot}029 \log [Pb'']c$ being independent of variations of [Pb''].

Hence—

$$\log [Pb_x(NO_2)_y] = \log k + x\left(\frac{c-E}{0{\cdot}029}\right) + y \log [NO_2'] \quad . \text{(i)}$$

In a series of measurements to find $x$ the concentration of $NO_2'$ was kept sensibly constant by using a four times weight normal solution of sodium nitrite. Experiments already described have shown that [Pb''] is very small, hence—

$$[Pb_x(NO_2)_y] = \frac{1}{x}[M]$$

and $\log [Pb_x(NO_2)_y] = \log [M] - \log x.$

Equation (i.) therefore gives

$$\log [M] - \log x = \log k + x\left(\frac{c-E}{0{\cdot}029}\right) + y \log [NO_2'].$$

Hence for a constant value of $[NO_2']$ E is a linear function of log [M] and $x$ is given by

$$\frac{\delta \log [M]}{\delta E} = -\frac{x}{0{\cdot}029}.$$

Hence for such concentrations as satisfy the assumptions by means of which the foregoing equations have been derived the graph of log [M] expressed as a function of E is a straight line from which the value of $x$ can be found at once.

The following numbers were obtained, the lead anode being carefully cleaned before each measurement—

| E. | Log [M]. | [M] |
|---|---|---|
| 0·5481 | 2·8265 | $6{\cdot}706\times10^{-2}$ |
| 0·5511 | 0·7392 | 5·485 |
| 0·5531 | 0·6654 | 4·628 |
| 0·5560 | 0·5473 | 3·526 |
| 0·5628 | 0·3132 | 2·057 |

The straight line through these five points gives $x = 1{\cdot}03$

Hence the complex anion is of the form $Pb(NO_2)_y$.

A series of measurements were made to find $y$; [M] was maintained constant while $[NO_2']$ varied, but $[NO_2']$ was always much greater than [M], under which circumstances the concentration of the complex anion remained sensibly constant. Hence from equation (i.) E must be a linear function of $\log [NO_2']$ and therefore—

$$y = \frac{1}{0{\cdot}029} \cdot \frac{\delta E}{\delta \log [NO_2']} \quad . \quad . \quad . \quad . \quad \text{(ii.)}$$

If R ohms be the resistance measured when the conductivity cell is filled with one of the sodium nitrite solutions to be used, if $\eta$ denote the viscosity of this solution relative to pure water, if $R_\infty$ ohms is the resistance measured when the same cell is filled with a very dilute solution of sodium nitrite of concentration $c_\infty$ grm. formula weight per litre of solution, then $[NO_2'] = \eta R_\infty c_\infty \mid R$ where the degree of ionisation is assumed to be given by the Arrhenius formula.

Hence—

$$\log [NO_2'] = \log\left(\frac{\eta}{R}\right) + \log R_\infty c_\infty$$

and therefore—

$$y = \frac{1}{0.029} \cdot \frac{\delta E}{\delta \log\left(\frac{\eta}{R}\right)} \text{ . from equation (ii)}$$

This method of analysis is quite general and avoids the trouble of finding the resistance of solutions of great dilution, with the possibility

of large error due to hydrolysis. The graphical method of finding the partial differential coefficients makes it easy to see whether the limits of concentration, for which the equations are valid, have been passed.

The solutions of sodium nitrite employed for finding $y$ were of concentrations 3, 3·5, 4, 4·5, 5 times weight normal.

*The viscosities relative to water at* 18° were found by means of a glass viscosimeter shaped somewhat as the instrument described by Washburn (*Jour. Am. Chem. Soc.*, 1913, xxxv., 739); the capillary was 19·5 cms. long, with internal diameter 0·0556 cm.; the volume of liquid flowing through the capillary for each experiment was approximately 6·7 cc; the specific gravities of the nitrite solutions were found relative to water at 18° by means of an Ostwald pyknometer.

| Normality of Solutions. | Time of Flow in Seconds. | Specific Gravity | Relative Viscosity $\eta$. |
|---|---|---|---|
| water | 1009 | | |
| 3 | 1168 | 1·1189 | 1·2953 |
| 3·5 | 1213 | 1·1374 | 1·3674 |
| 4 | 1264 | 1·1535 | 1·4450 |
| 4·5 | 1323 | 1·1681 | 1·5317 |
| 5 | 1378 | 1·1837 | 1·6166 |

The water used as standard of comparison was of conductivity $1·39 \times 10^{-6}$ reciprocal ohms; it was made from a good distilled water of conductivity about $7·8 \times 10^{-6}$ reciprocal ohms by boiling this latter briskly at 30° whereby the dissolved carbon dioxide was eliminated for the more part. This method was adopted at the suggestion of Col. Heycock.

*The resistances of the nitrite solutions* were found by Whetham's method, using a post-office box, galvanometer, and rotating commutator. The box and commutator were by Messrs. Pye. The commutator was driven so as to reverse the current 1360 times per minute.

| Normality of Solutions | Resistance R in Ohms | $\log\left(\frac{\eta}{R}\right)$ |
|---|---|---|
| 3 | 14·84 | $\bar{2}·9409$ |
| 3·5 | 13·72 | $\bar{2}·9985$ |
| 4 | 12·96 | $\bar{1}·0473$ |
| 4·5 | 12·46 | $\bar{1}·0896$ |
| 5 | 12·06 | $\bar{1}·1273$ |

*The electromotive forces* of the combinations made from these solutions were measured, when each contained the same small total concentration of lead. Pure lead nitrite was prepared, and, as a preliminary series of experiments made it seem probable that the value of $y$ was 4, both lead nitrite and sodium nitrite were added to each solution, for every grm. formula weight $Pb(NO_2)_2.H_2O$ added to a solution two grm. formula weights. $NaNO_2$ were also added

| Normality of Solutions. | E.M.F. in Volts. | $\log\left(\frac{\eta}{R}\right)$. |
|---|---|---|
| 3 | 0·5304 | $0·9409+\bar{2}$ |
| 3·5 | 0·5376 | 0·9985 |
| 4 | 0·5436 | 1·0473 |
| 4·5 | 0·5484 | 1·0896 |
| 5 | 0·5554 | 1·1273 |

If E be plotted as a function of $\log\left(\frac{\eta}{R}\right)$ it will be found that the points for the first four solutions lie almost exactly on a straight line but that the point for the five times normal solution lies off this straight line.

This may be due to an error of experiment; it seems curious that equation (ii) should be valid for concentrations of sodium nitrite up to 4·5 normal but be inapplicable to the 5 normal solution.

The straight line determined by the first four points gives $y=4·04$.

Hence the complex anion is of the form $Pb(NO_2)_4$ for solutions containing a total concentration of lead of the order $9 \times 10^{-2}$ grm atoms per litre of solution and for solutions of smaller concentration.

### *The Solids which can be obtained from the Anolytes of Various Concentrations.*

(i) A 1·5 times weight normal solution of sodium nitrite was used, the electrolysis was continued until 16 grms. of lead per 100 cc. of anolyte went into solution. By evaporation in an exhausted desiccator over concentrated sulphuric acid at a temperature of 16° to 18° large light orange yellow crystals were obtained

These had the reactions of a nitrite and of lead. The lead was estimated as sulphate. The percentage of lead found was 65·19, the calculated percentage of lead in $Pb(NO_2)_2.H_2O$ is 65·31.

Hence the crystals were lead nitrite.

This seems to be a good method of preparing pure lead nitrite.

(ii) A once weight normal solution of sodium nitrite was used and 8 grms. of lead per 100 cc. of anolyte were put into solution. In this case also crystals of the same appearance were obtained, the temperature during evaporation being 16° to 18°. The percentage of lead found was 65 22. Hence these crystals were lead nitrite.

(iii) A four times weight normal solution of sodium nitrite was used and 5 grms of lead per 100 c. of anolyte were put into solution. The temperature during evaporation was 16° to 18°. White crystals of sodium nitrite were obtained.

(iv) A four times weight normal solution of sodium nitrite containing 15 grms. of lead per 100 cc. of anolyte was treated as before, the conditions of temperature being the same. Crystals of sodium nitrite were again obtained.

An isothermal equilibrium curve could be constructed for the system lead nitrite—sodium nitrite—water by taking as abscissæ the weights of sodium nitrite per 100 grms. water and as ordinates the weights of lead nitrite per 100 grms. water. The results described in (i) to (iv) indicated that the curve might consist of three portions, the first portion representing solutions in equilibrium with lead nitrite as solid phase, the third portion solutions in equilibrium with sodium nitrite as solid phase and a middle portion representing solution in equilibrium with a solid which might be the sodium salt of a lead complex. A necessary condition for this would be that this solid phase should be stable at the temperature of isothermal evaporation in the presence of the liquid phase Solutions of the following initial concentrations were evaporated in an exhausted desiccator over concentrated sulphuric acid at 16° to 18°:—

(*a*) 4·5 times weight normal sodium nitrite containing 33 grms. of lead per 100 cc. of solution.

(*b*) Twice weight normal sodium nitrite with 12grms. of lead per 100 cc. of solution.

(*c*) Four times weight normal sodium nitrite containing 17 grms. of lead per 100 cc. of solution.

In each case crystals were obtained, but these were not homogeneous.

A further experiment was made with an anolyte four times weight normal with respect to sodium nitrite, the sodium nitrite was free from nitrate, the electrolysis was continued until the resulting solution contained 20 grms. of lead per 100 cc. This was evaporated isothermally in an exhausted desiccator surrounded with ice Crystals were obtained, but these also were not homogeneous.

It seems that under the conditions of the experiments just described no solid phase such as $Na_2(Pb(NO_2)_4)$ exists in stable equilibrium with nitrite solutions containing the plumbo nitrite complex.

*The Electrolysis of Solutions of Potassium Nitrite.*

It seemed possible that a potassium salt corresponding with the complex might be easier to isolate in the solid state. A series of experiments were made with solutions of potassium nitrite. Sticks of this material were used and therefore potassium nitrate was present in the solutions. The concentrations of the solutions were approximately normal, twice normal and four times normal by weight.

Just as with sodium nitrite the lead went into solution at the anode forming a complex which gave a bright orange colour to the anolyte, no gas was evolved at the anode, no trace of metal was deposited on the cathode. There seemed no reason to suppose that the lead complex in solution was other than that already described.

*The Solids Obtained from Potassium Anolytes.*

By evaporation in an exhausted desiccator over concentrated sulphuric acid crystals were obtained; these were transparent needles often four to five centimetres long, of a bright orange colour. Their appearance was homogeneous and suggested either a chemical individual or solid solutions.

When heated they evolved nitric peroxide and water; they gave the reactions of a nitrite, of lead and of potassium They always contained a nitrate; this was found by acting on an ice-cold concentrated solution of the crystals with excess of hydrazine sulphate added as a fine powder, filtering free from lead sulphate and then adding "nitron" acetate solution.

The results of analysis of various specimens of these crystals are tabulated: the lead was estimated as sulphate, the potassium as sulphate, the $NO_2$ by means of potassium permanganate, the $NO_3$ as "nitron" nitrate. The water was not estimated.

In the tables the first columns give the percentages of the metals and the acid radicals, the second columns give these percentages divided by the respective formula weights.

(i) From a normal solution of potassium nitrite containing 8 grms. of lead per 100 cc. after electrolysis :—

| | | | |
|---|---|---|---|
| $NO_2$ | 35·94 | 0·781 | |
| Pb | 48·11 | 0·232 | $[NO_2]/[Pb]=3·36$ |
| K | 13·30 | 0·340 | |
| $NO_3$ | 1·23 | 0·020 | |

(ii) From a twice normal solution of potassium nitrite containing 12·5 grms. of lead per 100 cc. after electrolysis—

| | | | |
|---|---|---|---|
| $NO_2$ | 36·55 | 0·795 | |
| Pb | 47·85 | 0·231 | $[NO_2]/[Pb]=3·44$. |
| K | 12·96 | 0·332 | |
| $NO_3$ | 1·10 | 0·018 | |

(iii) From a four times normal solution of potassium nitrite containing 5 grms. of lead per 100 cc. after electrolysis—

(*a*) First crop of crystals—

| | | |
|---|---|---|
| $NO_2$ | 37·82 | $[NO_2]/[Pb]=3·70$. |
| Pb | 46·06 | |

(*b*) Second crop of crystals taken from mother liquor of (*a*) twenty hours later—

| | | |
|---|---|---|
| $NO_2$ | 38·58 | $[NO_2]/[Pb]=4·15$ |
| Pb | 41·90 | |

(*c*) Third crop of crystals taken from mother liquor of (*b*) twenty hours later—

| | | |
|---|---|---|
| $NO_2$ | 39·43 | $[NO_2]/[Pb]=4·96$. |
| Pb | 35·80 | |

These results show that from solutions containing potassium nitrite, potassium nitrate and the plumbo nitrite complex a series of solid solutions can be formed in equilibrium with liquid phases. These solids are transparent crystalline bodies far less soluble than potassium nitrite and lead nitrite.

There is no evidence that definite chemical individuals of the nature of "triple salts" are produced.

Inasmuch as no lead was deposited on the cathode nor found in the catholyte during any of these electrolyses, the cationic complex ($KPbNO_3$) described by W. K. Lewis (*Dissert.*, Breslau, 1908) was not formed under the conditions of these experiments.

The percentage of $NO_3$ in the crystals obtained as described above was small An experiment was made to find whether similar crystals could be obtained from a solution containing a far higher concentration of potassium nitrate and also to test whether the complex derived from a sodium nitrite anolyte would behave in the same way as one derived from a potassium nitrite solution of approximately the same concentration.

*A twice normal solution of sodium nitrite* was electrolysed until it contained 12 grms. of lead per 100 cc. Potassium nitrate was added to this so that every 100 cc of the anolytes dissolved 10 grms. of the nitrate.

Crystals of precisely similar appearance were obtained under the same conditions of evaporation. Two crops were analysed, the second being taken from the mother liquor of the first some forty hours later.

| | | | | |
|---|---|---|---|---|
| (*a*) | $NO_2$ | 26·90 | 0·585 | |
| | Pb | 41·46 | 0·200 | $[NO_2]/[Pb]=2·92$. |
| | K | 15·65 | 0·400 | |
| | $NO_3$ | 14·79 | 0·238 | |
| (*b*) | $NO_2$ | 24·74 | 0·538 | |
| | Pb | 40·72 | 0·197 | $[NO_2]/[Pb]=2·74$. |
| | K | 15·53 | 0·397 | |
| | $NO_3$ | 17·27 | 0·278 | |

A series of solid solutions is formed here also.

*Discussion of Results and Summary.*

The plumbo nitrite complex is $(Pb(NO_2)_4)''$ for small concentrations of lead in alkali nitrite solutions. The anode potential measurements for increasing current make it probable that this is the only complex formed; if a second species of complex derived from $Pb(NO_2)_2$ and $NO_2$ ions were formed, the anode potential should be different from what it is with $(Pb(NO_2)_4)$ for the same total concentration of lead owing to difference in degree of dissociation of the complex anion; such a difference in the nature of the reaction of the anode would probably be accompanied by an abrupt change in curvature of the anode potential—current curve: the measurements given above afford no indication of such a change.

The solid in equilibrium with solutions obtained from anolytes of certain concentrations is lead nitrite crystals $Pb(NO_2)_2.H_2O$. The colour of these crystals is approximately the same as that of the solutions from which they are derived, it is not that to be expected from a consideration of the majority of salts derived from divalent lead. If, however, the plumbo-nitrite complex maintains its identity in these crystals, their colour is that which is probable from their origin.

It seems that a direct way of testing this hypothesis would be by an X-ray analysis of the crystals; the $(Pb(NO_2)_4)$ group should form a pattern regularly repeated in three dimensions relative to the cationic Pb atoms its identity being as well defined as that of the $CO_3$ group in a crystal of $CaCO_3$, which latter has been shown by the investigations of Prof. W. L. Bragg.

The solid solutions obtained from aqueous solutions containing the ions K, $NO_3$, $NO_2$, and the plumbo-nitrite complex are also coloured orange but more red than the orage of lead nitrite. It may well be that the complex exists as a definite atomic group in these crystals also.

Lead forms compounds in which it is divalent and others in which it is tetravalent. The complex formed in these electrolyses is derived only from divalent lead. Silver and copper anodes also give anionic complexes with $NO_2$ ions derived in each case from metallic ions of only one valency. Nevertheless it is possible for electricity to pass from the anode to anolyte with the simultaneous formation of complexes derived from two species of metallic ions. A gold anode with nitric acid as anolyte gives an example of this (*Faraday Soc. Trans.*, 1916, xi, 172): when the acid is concentrated both auric and aurous anionic complexes are formed; below a certain concentration only auric anions are obtained. It is intended to examine the reaction of a gold anode with sodium nitrite solutions to see if similar effects are produced.

Further experiments are in progress with other metals and nitrite solutions.

I am again much indebted to the Goldsmiths' Reader in Metallurgy, Col. C. T. Heycock, M.A., F.R.S. The admirable facilities he has given me, his continued interest in the course of the experiments, increase my gratitude to him for the privilege of working in his department.

The Goldsmiths' Metallurgical Laboratory,
Cambridge.

## THE "THERMOS" FLASK IN THE CHEMICAL LABORATORY.

By CLAUDE W. BOURLET and WALTER THOMAS.

It is not, apparently, generally recognised how useful an ordinary Thermos flask may become in the laboratory.

The Dewar vessel is, of course, universally employed for the storage of liquefied gases and other liquids boiling at low temperatures, or in other experiments where the maintenance of low temperatures is desirable. Chemists, however, do not appear to have exploited to the full the power of the vacuum flask of maintaining substances at temperatures above the normal.

This note will endeavour to point out a few cases in which this property may be utilised.

(1) *Reactions between liquids at elevated temperatures.*—Providing the reaction is not too strongly exothermic, it may be carried out conveniently in a Thermos flask or Dewar vessel. The mixture of liquids is heated to the desired temperature, poured into the insulated chamber, and left till the reaction is complete. This technique has been found particularly useful in the oxidation of organic compounds with $KMnO_4$. The same method—with appropriate modification—is obviously applicable to solid-liquid reactions. If gases are evolved, a vent must be provided.

(2) *The separation of emulsions.*—Oil-water emulsions and similar mixtures are conveniently "split" by warming and standing over night in a Thermos flask.

(3) *The separation of colloidal and flocculent precipitates.*—Flocculent precipitates "settle out" much more rapidly at elevated temperatures. Similarly, colloidal precipitates (*e.g.*, $BaSO_4$) become granular and easily separable by the same treatment. The technique is obvious.

(4) *Colour reactions.*—In certain colour tests," (*e.g.*, the Halghen reaction) the colour is only developed at temperatures above normal. In this case too, the vacuum flask becomes a great space and labour saver.

(5) *Reactions in gelatinising media.*—Occasionally it is necessary to carry out reactions in media which gelatinise or become extremely viscous at ordinary temperatures. Here again, the Thermos flask can replace the more cumbersome water-bath with advantage.

Finally, it may be pointed out that—at a pinch—a portable incubator for bacteriological work may be improvised from the ever-useful Thermos.

The Bourlet-Thomas Research Laboratories,
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United Kingdom and U.S.A. representing the following interests: British Government Department; U.S. Bureau of Standards; Referee Analysts—Independent; Railway Analysts—Representing users issuing specifications; Works Analysts—representing makers and users.

The standard figures are as follows:—

*Carbon Steel* "A2."

| | |
|---|---|
| Carbon (combined) | 0·039 |
| Silicon | 0·036 |
| Sulphur | 0·020 |
| Phosphorus | 0·008 |
| Manganese | 0·043 |
| Arsenic | 0·031 |
| Nickel | 0·06 |
| Chromium | 0·013 |
| Copper | 0·065 |
| Oxygen | 0·04 |
| Iron (by difference) | 99·64 |

The standard turnings may be obtained in 500, 100, or 50-grm. bottles, either direct from Organising Headquarters, 3, Wilson Street, Middlesborough, or through any of the leading laboratory furnishers at a price just sufficient to cover the cost. A certificate giving the names of the analysts co-operating, the types of methods used, and a detailed list of the results, will be supplied with each bottle.

## A NEW PROCESS FOR HYDROGENATION OF ORGANIC COMPOUNDS AND MORE ESPECIALLY FATS AND OILS.

THE essential feature of this process invented by A. Granichstadten and Dr. E Sittig is the employment of a double silicate of magnesium and nickel, a compound which gives remarkably good results. In hydrogenation with this catalyser, the oils, even at a temperature of only 35 to 40° Celsius, acquire an unusual degree of whiteness. With most of the known methods, the dark oils utilised for alimentary fats must be first or subsequently bleached, the oils hydrogenated by the new process are perfectly white, and ready for manufacture of alimentary fats.

The catalyser is prepared by precipitation of the double silicate so as to obtain as uniform a product as possible. Judging from the results of experiments, this process will soon occupy a high rank amongst those now utilised. Applications for patents have already been made in most countries, and in some cases granted.—*Giornale di Chimica*, October, 1921.

## CHLORINE CELLULOSE.

THE analytic method, given by Cross and Bevan, to separate and estimate cellulose in plants, boiling the fibrous matter with a diluted solution of sodium hydrate, then, after washing, treating it with gaseous chlorine, and finally with a boiling alkaline solution, this method, suitably adapted, has passed out of the laboratory into industry. The problem was solved by an Italian inventor, Beniamino Cataldi, who, after long study and experiments, took the first patent in 1915 for a process to manufacture cellulose with humid gaseous chlorine, this being followed by two others. In this same year, 1915, a company was formed for construction of an experimental works on an industrial scale at Polonghera (Cuneo), this company being subsequently transformed into the Societa Anonima Cellulosa, Polonghera. A very pure, white cellulose is now obtained from poplar wood, more highly appreciated that that made by the soda process. There is a considerable consumption of chlorine, 28 parts of chlorine per 100 of dry poplar cellulose. Manufacturers of electrolytic soda have long been looking for new markets for chlorine, and the Soc. Elettrochimica Pomilio has now decided to construct a plant at their Naples electrolytic soda works to produce about 10 metric tons of cellulose daily from hemp and Tripolitan esparto. Italy now imports about 800,000 quintaux of cellulose yearly, for which 250,000 of chlorine could be utilised, with the possibility of producing about 280,000 of electrolytic soda, thus meeting all the home requirements of caustic soda. Consequently, adoption of the Cataldi process on a large scale would make imports of cellulose and caustic soda unnecessary. *Giornale di Chimica*, October, 1921.

## CONTRIBUTION TO THE SOLUTION OF THE NITROGEN PROBLEM.

THE possibility of recovering a greater proportion of the nitrogen in coal is discused by Sig. G. Gianoli in the *Giornale di Chimica*, who reviews the technical difficulties relating to the distillation of gas in presence of alkaline chlorides or others (Riedel, German patent 298603).

For this process, in fact, all the plant for gas manufacture would have to be radically altered. The nitrogen of coal could thus be totally obtained, it is true, in form of $NH_4Cl$, but the expenses for alterations in gas works and coke ovens would be very great. The chlorides and hydrochloric acid produced would corrode the condensers and the gas itself contain hydrochloric acid detrimental to heating and lighting appliances. Then the coke would contain a great percentage of mineral matter. The process seems more suitable for poor gas plant.

To conclude, the question of utilisation of the nitric oxide produced in internal combustion engines is examined. Wittfield considers that this could be utilised. This is a new argument in favour of complete distillation of fuels such as lignite and peat in electric works.—*L'Engrais*, November 4.

## PROCEEDINGS OF SOCIETIES.

### THE FARADAY SOCIETY.

AT the Annual General Meeting of the Faraday Society held on December 13, the following Officers and Council were elected to serve for the forthcoming year. *President*—Prof. Alfred W. Porter, F.R.S. *Past-Presidents.*—J. Swinburne, M.Inst.C.E., F.R.S.; Sir R. T. Glazebrook, K.C.B., F.R.S.; Sir Robert A. Hadfield, Bart. *Vice-Presidents.*—W. R. Cooper; Prof. C. H. Desch; Prof. F. G. Donnan, C.B.E.,

F.R.S.; Dr. J. A. Harker, F.R S.; E. Hatschek; Prof. T. M. Lowry, C.B.E, F.R.S.; Dr. G. Senter. *Treasurer*—Robert L. Mond. *Council*—Prof. A. J. Allmand; Dr. H. Borns; Cosmo Johns; Prof. J. R. Partington; C. C. Paterson; Dr. J. N. Pring; Prof W. C. McC. Lewis; Prof. A. O. Rankine; Dr. E. E. Rideal; Sir Robert Robertson, K.B.E.

The Annual Report presented at the Meeting stated that during the year under review, four General Discussions had been held, three of them in co-operation with other societies, and that reports of the proceedings of these Discussions had been published and were in considerable demand.

The work of the Society had greatly expanded and an appeal was made for an increased membership, without which it would be difficult for the Society to keep pace with its increasing acitivities without a higher subscription. Up to the present this has been avoided.

## THE OPTICAL SOCIETY.

A Meeting of the Optical Society was held at the Imperial College of Science and Technology on Thursday, December 8, 1921, when the following papers were read and discussed:—

*"The Physical Meaning of Spherical Aberration."* By L. C. Martin.

Experimental determination of the intensity of light near the focus of a lens system showed that the "spurious disc" appearance persisted at the best visual focus, even in the presence of large amounts of aberration. The effect of increasing aberration is to draw light from the central concentration and scatter it in the surrounding field, and, from measurements of the loss, the necessity of restricting the phase residuals to within $\lambda/6$ is inferred. Spherical aberration is found to produce marked asymmetry on each side of the focus, a matter of great importance in some optical instruments.

*"An Auto Stroboscope and an Incandescent Colour Top."* By Dr. F. L. Hopwood.

A description was given of some novel optical phenomena which may be observed when revolving incandescent filaments are viewed. The production of a variety of stationary dark images, due to the eclipse of an incandescent wire by an adjacent cold wire or opaque object, when both are revolving round a common axis, was described, and it was shown how the phenomena might be practically applied to the study of the behaviour of a rotating body, by converting such a body into an auto stroboscope.

A demonstration was given of the use of a spinning incandescent electric lamp as a colour top and for exhibiting after image effects.

*"Achromatic One-Radius Doublet Eyepieces."* By Lieut.-Col. J. W. Gifford.

Eyepieces both of the Huygenian and the Ramsden types have been constructed from pairs of one-radius achromatic doublets with external plane surfaces to the flint lenses They compare well with the German orthoscopes in definition, while the cost of production, since the same radius serves for each doublet, or in the case of the Ramsden throughout, is sensibly less. Such eyepieces are adapted either for the telescope or the microscope. By their use a much more perfect achromatism is obtained, and also in both of them a flat field, and in one of them a very extensive flat field, likely to be useful in such operations as counting blood corpuscles, etc.

# CORRESPONDENCE.

## GERMAN REPARATIONS IN KIND.

*To the Editor of the Chemical News.*

Sir,—I enclose for favour of publication a copy of a letter addressed to the Prime Minister on the 9th instant by the Council of the Institution of Elecrical Engineers, on the subject of "German Reparations in Kind"—I am, &c.,

P. F. Rowell, *Secretary.*

The Rt. Hon David Lloyd George, O M., P.C., etc., First Lord of the Treasury, The Treasury, Whitehall, S.W. 1.

Sir,—The Council of the Institution of Electrical Engineers have had their attention directed to certain public declarations and Press communications proposing that the German Reparation Indemnity should be partly provided by the construction in this country of generating stations and the carrying out of railway electrification by German contractors; and having appointed a Committee to report to them thereon, desire to put before the Government their considered view on these proposals as follows:—

On the general principle of reparations in kind they have to remind the Government that at the present time when unemployment is so extensive any reparations in kind should be of such a nature that they do not compete with any productions in this country involving employment on a great scale of labour both skilled and unskilled.

With regard to the proposals that large electric power stations should be erected and that railway electrification should be undertaken by German contractors, they desire to make the following observations. It is possible that the proposals for the acceptance of German plant on account of reparations may have existed from a hasty impression that such action would confer benefits on this country in the form of cheaper transport and power. But if such plant is to stand as a contribution towards reparations, its value must be debited to the undertakings using it. In no other way can such value be put to the credit of National indebtedness There is, therefore, no good reason to suppose that the use of German plant obtained in that way would result in the users of it being able to give a cheaper service than with new equipment of British manufacture.

There are, however, other considerations which my Council desires to urge. The Electrical industry in this country is at the present time suffering from a grave lack of employment in all its branches, but nevertheless many works are being run in the expectation of a trade revival. Should it be decided to accept German machinery on a large scale, there is no doubt

that a large additional amount of unemployment would immediately result, and that both the work-people and technical staffs at present being kept together would be disbanded. Moreover, the effect of the acceptance for the public service of this country of electrical machinery of German manufacture would be a world-wide advertisement for such goods, and would fatally diminish the present prestige of British electrical goods with most serious effects on our export markets

The experience of the war showed the necessity of this country having a large number of highly skilled and trained electrical engineers available, and the members of the Institution of Electrical Engineers were called upon during the war to undertake work for the national forces requiring the highest skill.

A proposal which would have the effect of crippling many of the most important electrical manufacturing concerns and leaving this country dependent for electrical services upon German industry would result in discouraging the training of electrical engineers for what, in war time, is a vital necessity.

In view of the points briefly set out above, the Council of the Institution of Electrical Engineers representing all branches of the Electrical industry, desire to urge most strongly on H.M. Government the disastrous consequences which would ensue to the industry if electrical construction in this country on an extensive scale is entrusted to German manufacturers. Any possible immediate advantage anticipated by the proposers of the scheme of reparation could not offset the ruin of those industries in this country which are engaged in the manufacture of steam turbine plant and heavy electrical machinery, both of which had their sole origin in British science and inventiveness.

The Council of the Institution trust that in view of the discussions which have been published, H.M Government will remove the great uncertainty which has been created in the industry by an immediate statement that such proposals will not be entertained. If, however, proposals of the kind should be considered by the Government, my Council ask that they should be given an opportunity of being heard by yourself or the Chancellor of the Exchequer before any action is taken.—I am, &c.,

(*Signed*) J. S. HIGHFIELD, *President*

## NOTES.

ROYAL INSTITUTION.—The Christmas Lectures adapted to a juvenile auditory will be delivered by Prof. J. A. Fleming on "Electric Waves and Wireless Telephony" on the following dates, at 3 p.m : Thursday, Dec. 29, Saturday, Dec. 31, Tuesday, Jan. 3, 1922, Thursday, Jan. 5, Saturday, Jan. 7, Tuesday, Jan. 10.

THE *Journal of the Society of Chemical Industry* for December 15 reproduces an Address delivered by Mr. G. C. Clayton at the Liverpool Section in October last on "Sulphuric Acid Manufacture"; at the conclusion of the Address a few words are given on future prospects which are so hopeful that we take the liberty of reproducing them. "*Prospects.*—With regard to the future, I am unable to take the pessimistic view that our industry will not recover. Dark and uncertain as the future appears at the moment, we must not lose hold of the essentials of our success What was the position before the war? Industrially, judged from the standpoint of foreign trade, we were apparently in an unassailable position; but it was evident then that the lethargy engendered by a surfeit of prosperity had to be shaken off if we were to maintain our position. But the fact remains that we had achieved that position and held it so long for certain very clear and well-understood reasons. First, we owed it to our geographical position—the clearing house of the old and the new worlds—which made us the trading, banking, and carrying nation of the world. Secondly, we had readily accessible and cheap supplies of coal and iron; withal we were exempt apparently from the dread possibility of Continental warfare, with no great military commitments, and with our huge trade, taxation was comparatively low. But even more important than these, we had the solid British character—loyal, persevering, and conscientious. We were the great colonisers of the world; we were in consequence constantly opening up new spheres of influence which meant new markets for the industries of the country, and we were able, under humane and economic conditions, to produce at costs which could compete with those of other countries. If we are to continue as an industrial country, costs of production must come down; but that does not necessarily mean that wages must be drastically reduced to below pre-war rates, or that the standard of living need be lowered. What must be reduced is the cost of the unit. There must be more production per man, and the greater the production the greater the efficiency, and the greater the chance of success. Our industry is of vital importance to the country. Its necessity was proved during the war; it is equally vital in times of peace. We must keep all our industries in the forefront, and we must largely depend on our chemists to do this, not only in the chemical industry, but in practically every other No up-to-date works can afford to be without its chemist, and no chemist is of use unless he continues to study throughout his life."

THE BRITISH TRADE SHIP.—We have already called attention to the project of a floating exhibition that is to carry British productions to the chief business centres of the world. The preliminary arrangements are progressing rapidly and from a budget of particulars just to hand, we are pleased to learn that the costs of production are so far altered that the promoters of the enterprise are able to reduce charges by 33⅓ per cent on account of the fall in costs of British manufacture. This certainly foreshadows a revival of trade, and there are many other indications pointing to the same end, which we sincerely hope will continue unchecked.

HOSPITAL SUPPLIES PURCHASE BOARD.—The setting up of a Hospital Supplies Purchase Board appears among the recommendations of the New Zealand Hospitals Commission which was appointed to inquire into and report upon

proposals to amend the New Zealand Hospitals and Charitable Institutions Act of 1909. By this means it is believed large economies would be effected through the buying in bulk of drugs and dressings for the whole of the hospitals of the Dominion. The Commission recommended that this Board should include officials from the four base hospitals who have had large experience of buying, two business men, and representatives of the Health and Mental Hospitals Departments. H.M Trade Commissioner in New Zealand (Mr. R. Dalton) has informed the Department of Overseas Trade that it has been definitely decided to establish a purchase board on these lines although this has not yet been done. It is probable also that buying agents will be appointed in London.

We have received from the Controller of H.M. Stationery Office a copy of the Report of the Discussion on the "Physics and Chemistry of Colloids" held jointly by the Faraday Society and the Physical Society of London. It is a well-printed and very fully illustrated pamphlet of 190 pages, and gives full details of this most important contribution to the knowledge of colloidal physics and chemistry. Interesting papers were contributed by Professors Svedberg, Pauli, Hatschek, Sir Robert Robertson, Dr. Morris Travers, Sir Herbert Jackson, and many other well-known workers in the field. There is an appendix dealing with the Proteins and Colloid Chemistry by Jacques Loeb, and another on the Internal Pressure of Liquids by H. Kneebone Tompkins. Copies of the Report are obtainable at H.M. Stationery Office, Imperial House, Kingsway, price 2s. 6d. net.

Grants for Scientific Research in Norway.—In connection with the proposed establishment of funds for scientific research in Norway, H.M. Minister at Christiania reports that grants have now been made for the following purposes: (1) 8000 kroner for experiments to be made in connection with the use of acetylene gas as motor fuel; (2) 24,000 kroner for the purpose of investigation in vitamina with special application to cod-liver oil; (3) 6000 kroner to examine the possibility for employing calcium carbide as a basis for further manufacture in Norway.

The London correspondent of the *Manchester Guardian Commercial*, in a recent issue says: "On good authority I hear that the railway managers have decided to make a substantial reduction in their charges for goods traffic, and that the lower scale will come into operation next month. An official announcement will, I understand, be made in a few days. Passenger fares have also been under consideration, but up to the present no decision has been reached, according to my information. Within the last fortnight representations have been made by a number of commercial organisations for a reduction of railway charges, and several meetings of the managers have been held to consider matters. As I mentioned some weeks ago, certain recommendations were made to the Boards of the various companies, but the directors, with dividends in mind, sent the proposals back to the Railway Clearing House for further consideration on certain points. These, I understand, have now been cleared up, hence the likelihood of early reductions."

## New Patents.

This List is specially compiled for the *Chemical News* by Messrs Rayner & Co, Registered Patent Agents, of 5, Chancery Lane, London, W C 2, from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously

*Latest Patent Applications.*

32152—Calvert, G.—Manufacture of substances containing a methyl radicle November 30.

32234—Imray, O. Y.—Manufacture of B-thionaphthisatin. Dec. 1.

32504—Laing, B.—Manufacture and utilization of formic acid. December 3.

32335—Plausons (Parent Co.).—Concentration of solutions of colloidal dispersions. December 2

31818—Strubell, A—Process for obtaining partial antigenes of pathogenetic bacteria non-resistant against acids. November 28.

32216—Weyman, G—Neutralization and drying of sulphate of ammonia. December 1.

*Specifications published this Week.*

163018—Lilienfeld, L. Manufacture of ethers of carbohydrates having the emperical formula $nC_6H_{10}O_5$ such as cellulose, starch, dextrine and the like.

163271—Lilienfeld, L.—Process for the production of oily bodies of high boiling point from aromatic hydrocarbon mixtures.

171722—Cornelius, C. R.—Process of producing zinc or zinc and lead.

171751—Heinemann, K and Hoesch & Co.—Process for the recovery of pure caustic alkalies from impure lyes.

165759—Hirschel, W. N—Process for the manufacture of phosphoric acid

150962—Goldschmidt Akt Ges.—Proc ss and appartus for the production of alkali sulphate and hydrochloric acid.

*Abstract Published this Week*

*Fluxes*—Patent No 170343.—A Flux for aluminium has been invented and Patented by Mr. H. V A. Briscoe, of 32, Blenheim Gardens, Cricklewood, and Richardson, D, of 26, Winterbrook Road, Herne Hill, of the District Chemical Co. Ltd., 1, Fenchurch Avenue, London. The flux which is particularly intended for the autogenous welding of aluminium, comprises one or more alkali halides and an activating agent which reacts with them, only in the presence of aluminium oxide. An alkali pyrosulphate or pyrophosphate is employed as activating-agent, a suitable mixture being potassium chloride 45 per cent, sodium chloride 30 per cent, potassium fluoride 7 per cent, lithium chloride 15 per cent, and the pyrosulphate or pyrophosphate 1 to 10 per cent. The materials are all melted together in a vessel free from metallic oxide soluble in the flux and on solidifying a homogenous mass remains which is powdered.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

# NOTICES.

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THE CHEMICAL NEWS.
VOL. CXXIII., No. 3220.

# CHEMISTRY: THE EVOLUTION OF MATTER.*

By FRANK WIGGLESWORTH CLARKE,
U.S. Geological Survey.

DURING the greater part of the nineteenth century many philosophical chemists held a vague belief that the so-called chemical elements were not distinct entities, but manifestations of one primal form of matter, the *protyle*, as it was sometimes termed. Other chemists, more conservative, looked askance at all such speculations, and held fast to what they regarded as established facts. To them an element was something distinct from all other kinds of matter, a substance which could neither be decomposed nor transmuted into anything else. One fact, however, they ignored, namely, that the elements were intimately connected by many relations, which are best shown in the periodic law of Mendeléeff, who actually predicted the existence of unknown elements which were afterwards discovered This is ancient history, with which all chemists are now familiar. It became evident to most chemists that the elements must have had some community of origin, for otherwise their relations to one another are unintelligible.

In 1873 I ventured to publish the suggestion (F. W. Clarke, "Evolution and the spectroscope", *Pop. Sci. Mon.*, January, 1873), based on spectroscopic evidence and assuming the nebular hypothesis to be true, that the evolution of the planets from nebulae had been accompanied by an evolution of the chemical elements. The nebulae are chemically simple, the hotter stars more complex, the cooler stars and the Sun still more so, and the solid earth the most complicated of all. This was promptly denounced as heresy; but nearly a year later Lockyer (N. Lockyer, *Proc. Roy. Soc.*, xxi., 513. Paper dated Nov. 20, 1873), put forth an analogous suggestion, based upon the same sort of evidence, but starting from the other end. That is, he assumed that in the hotter stars some elements were dissociated, and his suggestion was received with a good deal of favor. The heresy was beginning to be orthodox. In course of time the discovery of radioactivity by Becquerel and of Radium by Madame Curie established the fact that some, at least, of the elements were really unstable. The evolution of helium from radium, discovered by Ramsay and Soddy, made the evidence for this instability complete; a derivation of one element from another had actually been observed.

These discoveries opened a new field of research; and it was soon found that the elements at the top of the atomic weight scale, namely, uranium and thorium, are spontaneously but slowly decaying, yielding more than thirty new substances which differ widely in the point of stability. To each one a half-life period is assigned, measured in some cases by thousands of years, in others by fractions of a second. Among these are two new varieties of lead; one derived from uranium, the other from thorium, which chemically are not distinguishable from ordinary or normal lead except by differences in their atomic weights and their specific gravities. The lead from thorium has an atomic weight about a unit higher, and that from uranium about a unit lower, than the atomic weight of normal lead. To this class of facts I shall refer later, as evidence in support of my arguments. That chemical elements can decay is the essential fact to be remembered.

That the chemical elements were formed by a process of evolution from the simplest forms of matter can hardly be doubted now, but the process is not yet ended. They were developed at high temperatures; but when a certain stage is reached in the cooling mass they began to combine with one another to form the new class of substances which are known as compounds. These, obviously, represent an advanced degree of complexity, with corresponding instability; and with varying conditions both combinations and decompositions, such as are reproducible by human agencies, constantly occur. By this extension of the evolutionary process the solid Earth was built up, but in principle the process is the same throughout. From the formation of the first elements to the chemical changes now taking place upon the Earth there is no real interruption. One line of progress has been followed until a maximum of natural complexity and instability is reached in the organic compounds which form the basis of all physical life, whether vegetable or animal. The same fundamental matter, governed by the same fundamental laws, appears from beginning to end of the evolutionary process.

Between the formation of an element and the formation of a compound there is, however, an apparent difference The first stage of the process was one which required a vast period of time, the second stage is marked with rapidity. The series of elements was slowly formed, and their rate of decay, as shown between uranium and lead, is also relatively slow. The formation and decomposition of compounds, on the other hand, is rapid; and in some cases their rate is measurable. The distinction is not absolutely definite, for some of the short-lived products of radioactive decay seem to be exceptions to the rule, which in general may be stated as follows: The process of the evolution is characterized by progressive acceleration, being slow at first, and becoming gradually more and more rapid. Its rate of acceleration may not be uniform but the general drift is clear. It follows the line from the simplest substances to the most complex. In all vital processes the ease and rapidity with which compounds are formed and developed is evident, and some of these substances are extremely complicated.

In any attempt to discuss the evolution of the chemical elements we have for guidance some facts and many analogies. That the most complex elements are unstable we have already seen, and it is suspected that all the others follow the same rule. Potassium and rubidium are feebly radioactive, which is an evidence of instability, and other confirmatory evidence will be cited later. Stability, however, is a relative term, and a substance which is stable under certain conditions

*Reprinted from the *Journal of the Washington Academy of Sciences*, Vol. xi, No. 13, July 19, 1921.

becomes unstable under others. The prime factors which determine external stability are temperature, pressure, and chemical evironment. For example, some compounds which are stable in anhydrous surroundings are decomposed in presence of water. Calcium carbonate, under ordinary conditions, is divided at high temperatures into carbon dioxide and lime, but heated in a steel bomb it not only remains undecomposed, but it may even be melted, to form upon cooling a crystalline marble. Examples like these might be multipled indefintely. As a rule stability diminishes with increasing temperature, but is favored by increased pressure. We may also assume that the more symmetrical an atom or compound is, the more stable it is likely to be. We are dealing now with compounds; but to the evolution of the elements the same general rules must apply.

Now, returning to our main problem, was the evolution of the elements a regular progression, such as might be represented by a smooth curve or a straight line; or was it irregular and quite independent of their order in the scale of atomic weights? To answer this question we must try to imagine what happened in the development of the larger masses, the nebulae and the stars. On this subject there is a plausible hypothesis which has been favored by many astronomers; namely that the nebula at first was relatively cool that the temperature gradually rose to that of the hottest stars, and then regularly declined to the end of the series, the solid planet. A baseous mass contracting under the influence of gravitation, became warmer; at its centre where the pressure was greatest, the increasing condensation generated still higher degrees of temperature, until a luminous nucleus was formed. As condensation went on with increasing intensities of pressure, the temperature continued to rise until the heat generated by compression was less than that lost by radiation into space, when cooling began. Although this hypothesis, in its crude form, is not universally accepted, it nevertheless gives a fair conception of that part of the evidence with which we are concerned. The process of evolution from cool to hot and then to cool again is fairly outlined. The nucleus of the original nebula has its modern representative in the Sun.

In all the foregoing discussion it has been tacitly assumed that the nebula from which the solar system was developed was similar in all essential respects to the planetary nebulæ. The latter, as shown by their spectra, consist mainly of hydrogen, helium, and nebulium, with slight traces in some of them of carbon, nitrogen, and perhaps other elements. Nebulium is known only from its lines in the spectrum, and its atomic weight has been estimated by Fabry and Buisson as 2·7, placing it between hydrogen and helium. In any further study of relations between the atomic weights of the elements, nebulium must be taken into account, and perhaps also coronium, so called from its lines in the spectrum of the solar corona. From its position in the corona it is assumed to be lighter than hydrogen, and so would seem to be an even more primitive element. That possibility cannot be considered here; we must limit ourselves to the conditions actually seen in the nebulæ. No assumption is made as to the possible ancestry of the nebular elements They are the visible beginnings.

Now it is easy to see that in the process of evolution from nebula to sun an orderly development of the elements could hardly have been possible. With changing temperatures, changing pressures, and changing environments, all the conditions required for a regular progression according to the order of the atomic weights were lacking. The order actually followed was that of relative stability. In the hotter stars only the most stable elements were formed, and naturally in the greatest abundance. Calcium (atomic weight 40) and iron (atomic weight 56) were among the earliest to appear, while the others, between helium (atomic weight 4) and iron, either came later or were developed at first in smaller quantities. As cooling went on more and more elements were generated, and in the Sun all the possible ones are presumably present. It is conceivable that elements of different stability may have been formed simultaneously, one in that part of the cooling mass where temperatures and pressures were highest, another further away from the centre under less rigorous conditions. This, however, is something which cannot be proved. If the three nebular elements were the raw material from which the other elements were built, their relative amounts must have been continually changing, and so as each new element appeared a new environment was established for all that followed. How far these changes may have affected the evolution of the elements it is impossible to say, but in the evolution of compounds similar conditions would be significant.

That some of the chemical elements are very abundant, and others comparatively scarce, is a familiar fact which bears directly upon the theory of evolution. Their relative abundance in known terrestial matter has been repeatedly computed, by several workers and by different methods The results agree remarkably well, at least in the orders of magnitude as expressed in percentages. This order, when we combine the figures for the lithosphere, the ocean, and the atmosphere, is as follows. First, oxygen, then silicon, aluminium, iron, calcium, sodium, potassium, hydrogen, and titanium, and these ten elements form at least 98 per cent of the whole. Only 2 per cent remains for all the other elements, some 80 or more in number. (The details of the most recent computation of the relative abundance of the elements will appear in a joint paper by Dr. H. S. Washington and myself, which is in course of preparation).

For present purposes this estimate is obviously defective, for it covers hardly more than a thin film on the surface of the Earth and says nothing about the Earth's interior. This objection is easily met if we take three facts into consideration. The Earth behaves like a huge magnet, it resembles a huge meteorite, and its mean density is double that of the rocks forming its crust. From these facts, and other quite minor considerations which need not be discussed here, we may fairly assume that the interior of the Earth contains a large proportion of metallic iron, and the quantity of it needed to give with the crust the mean density of the globe can be calculated. This has been done by others, and it now appears that in the Earth as a whole, iron predominates,

oxygen and hydrogen fall to subordinate positions while the order of the other elements is little changed. Probably nickel would appear among the first ten elements, but such a change will not affect our argument. Ten or eleven elements, all below 59 in atomic weight, exceed in abundance all the others. They are structurally among the simplest elements, and therefore, presumably the most stable.

These conclusions may now be applied to the hypothesis of evolution. The total amount of matter in the original nebula was of course finite; a large part of it was absorbed in building the simpler and more stable elements, and only what remained was available for the development of all the others. This conclusion, I admit, is largely speculative, but it is a legitimate interpretation of evidence. It may be modified by future investigations, but it is not likely to be completely overthrown. It is possible that the relative abundance of the elements may be different in different parts of the solar system, but it is not probable that any of the higher elements can find a place among the first ten. The whole scheme of evolution may be figured diagrammatically as a series of waves in which the crests represent the elements, and the depressions the gap between them. In such a series the waves would reach their greatest height at iron, and then gradually flatten until the end where instability becomes most clearly evident.

Between the evolution of the elements and their degradation there is a sharp contrast. The two processes do not follow the same path. Uranium does not decay to thorium, that to radium, then to lead, and so on down the line. The same divergence is shown between the synthesis and decomposition of compounds. It would be easy, for example, to effect a direct synthesis of calcium carbonate from its elements; but to reverse the process without the intervention of other substances would be extremely difficult. To cite a different example, trinitrotulene, the T.N.T. of recent warfare, is prepared by the action of nitric acid on toluene, a relatively slow operation. On the other hand, when T.N.T. decomposes it does so instantaneously, and the products are oxides of carbon, methane, water, and free nitrogen Something likes this happens in the decay of a radioactive element, but with a difference; uranium, thorium or radium decomposes atom by atom; T.N.T. flies to pieces in mass. The one process is slow, the other extremely rapid.

I have already specified the external conditions which determine the stability of an element or compound, but when we consider the atom by itself, internal conditions are more important. On the structure of atoms there is not as yet a complete agreement, and much remains to be done before the problem can be definitely solved. I cannot go into this subject in detail, but I may take it for granted that the conception of an atom as consisting of an electropositive nucleus attended by a few or many electrons of opposite sign, is well established. In such a structure symmetry would be conducive to stability, and any deficiency in that respect would be unfavorable. For a simple element, with few electrons, symmetry would be most easily attained, for a complex element with many electrons it would be more difficult. Furthermore, an atom to be stable must show an exact balance between the electropositive and electronegative charges. With a single ring or shell of electrons the force of attraction holding nucleus and electrons together should be strongest; with concentric rings of electrons the outer ones would be more loosely held, and the atomic structure should be weaker. This seems to be the case with uranium and its neighbours. Here the structures are the most complex, and the number of electrons greatest. In short, the conditions, internal and external, which determine stability are by no means simple, and some of them operate in opposite directions. They all agree, however, in favouring the evolution of the simpler elements and so render the fact of their greater abundance more intelligible.

When an atom of uranium decays, an *alpha* particle, which is an atom of helium, is first discharged, and with a very high velocity. By a succession of such discharges a series of products is generated, each one differing by four units in atomic weight from its predecessor. The atomic weight of helium is 4. Three of these products, omitting intermediate forms, are ionium, radium, and an "isotope" of lead. Ionium is isotopic with thorium, but not identical with it except in its purely chemical relations. The atomic weights are not the same. A similiar difference is found for the lead derived from radium, which differs from normal lead in having an atomic weight about a unit lower. The isotope of lead in the thorium series differs from the normal by about the same amount in the opposite direction. (For a discussion of the nature of isotopic lead see Clarke *Proc. Nat. Acad. Sci.*, 1918, iv., 181.) In short, the degradation path from uranium, and also that from thorium is approximately parallel to the path of evolution, but not identical with it. The short-lived products of radioactive decay might be described as the debris of exploding atoms. They do not appear in the ascending series of the elements.

For the elements below the radioactive group, that is, those of the lower aomic weight, some evidence of instability has recently been obtained Rutherford, by passing swiftly moving alpha rays through nitrogen, has observed a slight evolution of hydrogen, an indication that hydrogen is a constituent of the heavier and more complex element. Oxygen, treated in the same way, yields a product of different character, something which appears to have an atomic weight near 3. If, however, the value should be slightly lower, it would have a curious significance. Attention has already been called to the existence of nebulium, to which the atomic weight 2·7 has been provisionally assigned. This is very close to 2.666..., or $2^2/_3$ more precisely.

Now $2^2/_3 \times 6 = 16$, the atomic weight of oxygen, a relation which may possibly be experimentally verified. If the bombardment of oxygen were carried on for a long time it might yield a gas in which the spectral lines of nebulium could be detected; and if that were done it would be a step forward in the study of atoms. I offer the suggestion with some hesitation, but it seems to be worth considering. It affects a number of other elements of which the atomic weights are multiples of 16.

By a remarkable series of experiments F. W. Aston (*Science Progress*, 1920, xv., 212), has

obtained evidence which he regards as proof of the complexity of the atomic weights as determined by chemical methods. Powerful positive rays in a magnetic field were applied to a number of elements, which then gave what he terms their "mass spectra". These spectra show lines corresponding to whole number atomic weights, which represent, not the accepted values, but some higher and some lower. Chlorine gives two such lines, corresponding to atomic weights 35 and 37, and mercury gives at least six, ranging from 197 to 204. The last two figures, I may add, are near the atomic weights of gold and thallium, that of mercury being 200.6. These new lines, as interpreted by Aston, represent isotopes, and the accepted atomic weights are regarded as mere statistical averages. In other words the atomic weights known to chemistry relate to mixtures, and are not true constants.

I must here allow myself to indulge in a very obvious truism. Whenever new phenomena are discovered an attempt is made to interpret them, and to bring them into relations with other phenomena. But it does not always follow that the first interpretation is the only one possible, nor even that it the best. Now it seems to me conceivable, that the lines of Aston's mass spectra may really belong to decomposition products of the elements, produced by the disintegrating effect of the positive rays. This conclucion, I think, is more in harmony with chemical evidence than the one first proposed. It is, furthermore, sustained by the fact that the elements of high atomic weight seem to show as a rule more lines in their mass spectra than those low in the scale. The most complex elements should undergo the largest amount of disintegration. If the atomic weights as actually determined by the best modern methods are mere statistical averages of widely differing figures, then the elements must be regarded as variable mixtures, and uniformity could hardly be expected. This lack of uniformity would extend to all chemical compounds, which should vary in composition and also in physical properties; all chemical calculations would become inexact, and even the spectra of the elements would lose much of their significance. Chaos would rule instead of order.

In point of fact the evidence in favor of definiteness of atomic weight is much better than anything which has been adduced to the contrary. On that subject I could make a strong argument in support of my position; but I do not care to overload this paper with details. In discussing the evolution of the elements, and also their decay, I must take a pragmatic position and assume their integrity. Their evolution follows an upward path, with which the downward path of decomposition is approximately but not exactly parallel. The two paths, however, coalesce in the region of hydrogen, nebulium, and helium; and so the beginning and the end are the same. That hydrogen and helium are the chief constitutents of the elements as we know them is possible, as Harkins in a long series of interesting papers has attempted to show. I cannot accept all his conclusions as final, although he has at least discovered some interesting relations. Nebulium should not be left out of account.

On the mechanism of the process by which the elements were built up I have nothing definite to say. I can only ask questions. If a heavy atom, like that of gold or mercury, is formed from simpler atoms, how are the latter changed? What happens to their nuclei and their electrons? Is the structure of the carbon atom the same in graphite and in the diamond? Here the tetrahedral atom which plays so important a part in stereochemistry has to be considered. With compounds these problems become much more complicated, that is, if we try to explain them in terms of atomic structure. Among organic compounds we find isomers and polymers, and many of them contain a hundred or more atoms to the molecule. How are their electrons rearranged, and what are they doing? All these compounds, as I have already shown, are items in the general scheme of the evolution of matter, in which the question of atomic structure is fundamental. I have in this paper only touched the surface of a vast problem, but my imagination has never wandered far from evidence and reasonable analogies. Perhaps I have made suggestions which may lead others to the discovery of new truths.

## A HIGH PRESSURE DUE TO ADSORPTION AND THE DENSITY AND VOLUME RELATIONS OF CHARCOAL.*

PAPERS ON SURFACE ENERGY AND SURFACE FORCES.

By WILLIAM D. HARKINS and D. T. EWING.

### I.—*The Compression of Liquids by Charcoal.*

WHILE working on Problem 108 of the National Research Council in the year 1918, the writers discovered an interesting relationship, which is that the volume of different liquids adsorbed by the same charcoal increases in the same order as the percentage compression for a definite high pressure—such as twelve thousand atmospheres. Thus the charcoal seems to produce the same change in the volumes of liquids which penetrate it, as is given by a high pressure. In our preliminary report it was stated that while accurate calculations of the pressures which would have to be put upon these liquids to give the same percentage compressions, could not be made in the absence of data on an incompressible or very slightly compressible liquid, it seemed likely that the order of magnitude might be represented by twenty thousand atmospheres in excess of the internal pressure of the liquid. (It is obvious that the magnitude of the mean pressure decreases as the volume of liquid considered increases.) While there is nothing novel in the idea of the existence of such powerful adhesional forces at the surface of a solid, their experimental demonstration in such a direct way is somewhat remarkable, since the highest values for the internal pressures of liquids thus far experimentally demonstrated are 34 atmospheres with water at 24·4°, 39·5 atmospheres for ethyl alcohol at 22·5°, and 72 atmospheres for ether at 17·7°. (Donny, *Ann. chim.*

*Presented at the Philadelphia meeting of the American Chemical Society, September, 1919. This problem was suggested to the National Research Council by the senior author. The data for one charcoal with 11 liquids were published in February, 1920 (Harkins and Ewing, *Proc. Nat. Acad. Sciences*, 1920, vi., 49-56). The present paper is an abstract of a thesis presented to the University of Chicago in August, 1919, by D. T. Ewing, in partial fulfilment of the requirements for the degree of Doctor of Philosophy. Reprinted from *Journal of the American Chemical Society*, August, 1921.

TABLE I.—*Apparent Density and Pore-Volume Determinations for a Steam-Activated Coconut-Shell Gas-Mask Charcoal.* (Charcoal E 602; service time 47·2 minutes; $-\Delta v=0·058$ cc ). (Data at 25°).

| 1. Liquid. | 2. Apparent density. | 3. Pore volume 1 cc | 4. Per cent compressed 12000 atmospheres.* | 5. Surface tension, dynes per cm $\gamma$. | 6. Viscosity in absolute units $\eta$. | 7. $\frac{\gamma}{\eta}$ | 8. $b. \times 10^4$ |
|---|---|---|---|---|---|---|---|
| Mercury | 0·865 | — | — | 57·0 | — | — | — |
| Water | 1·843 | 0·534 | 20·51 | 72·8 | 0·0101 | 7200 | 14 |
| Propyl alcohol | 1·960 | 0·559 | 22·93 | 23·7 | 0·0223 | 1062 | 76 |
| Chloroform | 1·992 | 0·566 | — | 27·13 | 0·0057 | 4760 | 45 |
| Benzene | 2·008 | 0·568 | — | 28·88 | 0·0064 | 4510 | 54 |
| $p$-Xylene | 2·018 | 0·571 | — | 28·33 | 0·0064 | 4430 | 81 |
| Petroleum ether | 2·042 | 0·579 | — | — | — | — | — |
| Carbon disulphide | 2·057 | 0·580 | 25·75 | 31·38 | 0·0037 | 8480 | 34 |
| Acetone | 2·112 | 0·590 | 27·0 | 23·50 | 0·0033 | 7120 | 44 |
| Ether | 2·120 | 0·592 | 30·0 | 17·1 | 0·0024 | 7125 | 39 |
| Pentane | 2·129 | 0·593 | More than ether | About 15 | 0·0024 | 6200 | 65 |

*The solubility of gases in these liquids increases in *general* with the percentage of compression or the compressibility, but the order is not exactly the same. The values for the density and for the pore volume listed in this table are calculated on the basis of the incorrect assumption that the liquids are incompressible. The same values would be obtained if the liquids are compressible but are not compressed. The eighth column gives the values of $b$ of van der Waals' equation.

TABLE II.—*Apparent Densities of Eight Charcoals in Water, Mercury, and Various Organic Liquids.*

| Charcoal. | Liquid. | Apparent density | Mean apparent density. | Volume of carbon in 1 cc charcoal. | Volume of pores in 1 cc of charcoal. |
|---|---|---|---|---|---|
| Charcoal A | Hg | 0·843 | — | — | — |
| (Steam activated, coconut shell-charcoal: | Hg | 0·841 | 0·842 | — | — |
| impregnated with copper; service time=42·9 | $H_2O$ | 2·112 | — | — | — |
| minutes; $-\Delta v=0·052$ cc ). | $H_2O$ | 2·112 | 2·112 | 0·399 | 0·601 |
| | $C_6H_6$ | 2·291 | — | — | — |
| | $C_6H_6$ | 2·298 | 2·295 | 0·366 | 0·643 |
| | Ether | 2·432 | — | — | — |
| | Ether | 2·422 | 2·426 | 0·347 | 0·653 |
| Active carbon No 4 | Hg | 0·705 | — | — | — |
| (From anthracite coal and pitch; service time | Hg | 0·713 | 0·709 | — | — |
| =40·9 minutes; $-\Delta v=0·067$.). | $H_2O$ | 1·807 | — | — | — |
| | $H_2O$ | 1·809 | 1·808 | 0·392 | 0·608 |
| | Ether | 2·186 | — | — | — |
| | Ether | 2·172 | 2·177 | 0·325 | 0·675 |
| Charcoal No. 1 | Hg | 0·869 | 0·869 | — | — |
| (Air activated, coconut shell-charcoal; | $H_2O$ | 1·863 | 1·863 | 0·467 | 0·533 |
| service time 32 minutes; $-\Delta v=0·053$ cc.). | $C_6H_6$ | 2·014 | 2·014 | 0·432 | 0·568 |
| | Pet. Eth. | 2·042 | 2·042 | 0·421 | 0·579 |
| | Ether | 2·094 | 2·094 | 0·414 | 0·586 |
| E621 | Hg | 0·989 | — | — | — |
| (Air-activated, coconut shell-charcoal; service | Hg | 0·998 | 0·995 | — | — |
| time =27 minutes; $-\Delta v=0·051$). | $H_2O$ | 1·832 | — | — | — |
| | $H_2O$ | 1·838 | 1·835 | 0·542 | 0·458 |
| | Ether | 2·023 | — | — | — |
| | Ether | 2·029 | 2·026 | 0·491 | 0·509 |
| Active carbon No. 1 | Hg | 1·177 | — | — | — |
| (From anthracite coal and pitch; service time | Hg | 1·172 | 1·175 | — | — |
| =19 minutes; $-\Delta v=0·043$ cc.). | $H_2O$ | 1·936 | — | — | — |
| | $H_2O$ | 1·932 | 1·934 | 0·609 | 0·391 |
| | Ether | 2·076 | — | — | — |
| | Ether | 2·074 | 2·075 | 0·566 | 0·434 |
| Active carbon No 3 | Hg | 1·488 | — | — | — |
| (From anthracite coal alone; service time= | Hg | 1·492 | 1·490 | — | — |
| 11 minutes; $-\Delta v=0·018$ cc.). | $H_2O$ | 1·880 | — | — | — |
| | $H_2O$ | 1·872 | 1·876 | 0·799 | 0·201 |
| | Ether | 1·911 | — | — | — |
| | Ether | 1·902 | 1·906 | 0·781 | 0·219 |
| Laboratory charcoal | Hg | 0·521 | 0·521 | — | — |
| (From beechwood; service time=0·0 minutes; | $H_2O$ | 1·644 | 1·644 | 0·317 | 0·683 |
| $-\Delta v=0·004$ cc.). | Ether | 1·665 | 1·665 | 0·313 | 0·687 |
| Cedar wood | Hg | 0·817 | — | — | — |
| (Service time=0·0 minutes; $-\Delta v=0·008$ cc.). | Hg | 0·813 | 0·815 | — | — |
| | $H_2O$ | 1·497 | — | — | — |
| | $H_2O$ | 1·502 | 1·499 | 0·544 | 0·456 |
| | Ether | 1·504 | 1·504 | 0·536 | 0·464 |

*phys.*, 1846, xvi., 167; Berthelot, *ibid.*, [3], 1850, xxx., 232; Moser, *Ann. phys.*, [2], 1877, clx., 138; Helmholtz, *Ges. Abh.*, 1887, iii., 264; Worthington, *Phil. Trans.*, [A], 1892, clxxxiii., 355; Meyer, "Zur Kenntnis des negativen Druckes in Flussigkeiten," Halle, 1911. The heat of adsorption was discovered as a phenomenon by Pouillet nearly one hundred years ago (*Gilb. Ann.*, 1823, lxxiii., 356). The hypothesis that the high heat of adsorption indicates that it may be convenient to look upon adsorbed material as in a compressed state, is also very old. It is discussed in Freundlich's "Kapillarchemie," (Leipzig, 1909, p. 111) However, the work of the present writer gives the first direct experimental demonstration of this compression, and shows that the magnitude of the effect is much greater than has usually been supposed).

Our hypothesis that the compression of the liquid is due to a pressure of this order of magnitude at the interface liquid-charcoal, is supported by the very interesting work of Lamb and Coolidge (*Jour. Amer. Chem. Soc.*, 1920, xlii., 1146-70), who approach the subject from an entirely different experimental standpoint. They find that the net heats of adsorption are closely proportional to the heats of compression under high pressure, which "indicates that the liquids are all attracted by the charcoal with substantially the same force, and that the net heat of adsorption is merely heat of compression. The absolute value of this attractive force appears to be about 37,000 atmospheres when 1 cc. of liquid is adsorbed on 10 grms. of charcoal." Still another paper, also published later than our own, comes to the conclusion that the volume of a liquid in charcoal is different from the volume of the same mass of the same liquid in bulk. (A M. Williams, *Proc. Roy. Soc.*, December, 1920, xcviii.A., 223-34 The writer has not been able to consult this paper, since the number has failed to reach any of the Chicago libraries).

In March, 1920, Cude and Hulett (*Jour. Amer. Chem. Soc.*, 1920, xlii., 391-401; their results on benzene are affected by some factor which we have been able to duplicate) published data on the volume and density relations of one charcoal as obtained with four different liquids. It happened that at the time our preliminary paper giving data on eleven different liquids had been published, and we were somewhat disturbed to find that the agreement between the two sets of data was not as perfect as might have been desired, though the only discrepancy was for the single liquid benzene. However, on this account the publication of the present paper has been delayed for considerably more than a year. During this time Mr. C E. Monroe has repeated a number of the determinations, and has extended the investigation to other liquids for which the compressibilities have been determined by Bridgman. His results will be published in a separate paper, but it may be stated that they agree almost exactly with those of the present and also of the preliminary publicaion.

In the experiments presented here the charcoal was outgassed by the use of a mercury condensation pump with a large throat and connecting tube (25 mm. in diameter), but it was found necessary to constrict the tubes near the charcoal bulb to 1 cm. The apparatus first used was similar to that described by Lemon (*Phys. Rev.*, 1919, xiv., 283) since we had two sets of this apparatus for work on the speed of adsorption of various poison gases. However, such an elaborate apparatus is unnecessary for the work on liquids, and a system without stopcocks was found to be better for this purpose. The outgassing was first conducted at low temperatures, with a gradual increase to 600°. The tubes of charcoal were kept at the latter temperature from two to three days, or until the pressure registered by the McLeod gauge had fallen to 0·0001 mm. and had remained as low as this for at least six hours. This pressure was determined while the pump was still running, but the tubes of charcoal were connected to the main vacuum line (1·5 cm. in diameter) between the gauge and the pump. The neck of the bulb, which usually contained about 10 grms. of charcoal, was then sealed off to a point while the bulb was still kept hot in the electric furnace. The bulb was cooled, the point dipped under the surface of the hot liquid, and broken off, so as to allow the liquid to rise into the tube. The tube was weighed at intervals, being kept in a thermostat at 20·00°, except during the periods it was kept in the balance. The surface of the liquid was so adjusted in the thermostat that the lower part of the meniscus was exactly at a fine circular graduation made on the neck of the tube where it had been constricted to a capillary. After the drift had ceased, the final data as recorded, were obtained. The character of this drift has been treated by Cude and Hulett, and will be considered by Mr. Monroe, so only the final density data will be presented here.

### *II.—Apparent Density and Volume Relations of Charcoal.*

The most closely agreeing data were obtained by the use of a steam activated, coconut-shell, gas-mask charcoal E 602, which gave a service time of 47·2 minutes by the accelerated chloropicrin test. On account of the close agreement of the three or more density determinations with each liquid, in general to $\pm 0{\cdot}001$, only the average values will be included in Table I., which gives the results for this charcoal. The density listed in col. 2, and the pore volume given in col. 3, are not the real, but only the apparent values, calculated on the basis that the liquids are incompressible, or what amounts to the same thing in this case, that the liquids are not attracted by the charcoal sufficiently to cause any compression. Since apparently this kind of assumption is not justified, the true density and pore volume can be calculated only when the correct interpretation of the cause of the considerable variation shown in the Table, is obtained.

In order to understand the volume and density relations upon which the adsorptive properties of charcoal depend, it is important to obtain an idea of the structural relations of coconut charcoal, in so far as the latter can be revealed by the use of the microscope. The writers have about 60 microphotographs, with magnifications as high as 2000, prepared by Dr. Rheinhardt Thiessen of the U.S. Bureau of Mines, and these have been used in the present study of the pore volume relations Unfortunately none of these can be presented here, but reference may be made to three microphotographs reproduced in an earlier paper by Lamb,

Wilson, and Chaney (*J. Ind. Eng. Chem.*, 1919, xi., 420-38), which do not, however, represent all of the types of structure found. A reference to their Figs. 7 and 8 (pp. 428 and 429) of their paper will show that the lumps of charcoal contain many pores which are visible at a magnification of 732 diameters. Those visible at a magnification of 2000 may be called capillaries or macropores. The walls of carbon, which are represented by the light portions of the figure, are undoubtedly very porous, and contain an enormous number of "micropores" which are ultramicroscopic. A study of the photographs shows that the mean diameter of the macropores is about 12 microns (this diameter is dependent upon the methods of production of the charcoal). The micropores may be defined arbitrarily as those whose diameters are less than $10^{-5}$ cm. (less than 100 millimicrons), though vapour-pressure measurements indicate, in so far as they are of any value for this purpose, that they are mostly of the order of $10^{-6}$ cm. or less, in diameter.

Since mercury penetrates neither the capillaries nor the micropores, the density given in Table I. and II., with this liquid used to fill the "voids" between the lumps of charcoal, is that of the lumps themselves, walls, micropores, and capillaries included, or what is known as the lump or "block density." It will be seen that this density is close to 0·85 for two of the highly activated coconut-shell charcoals, but is considerably higher for the slightly activated charcoal E621, for which the value is practically 1·000. The density of the cedar wood charcoal, 0·815, is very nearly the same, yet this specimen shows an almost zero service time, while beech wood charcoal, also a very poor adsorbent, has a block density of only 0·521. The active carbon 4, with a moderately high service time of 40·9 minutes, has a moderately low density (0·709), and the much less active No. 1, also made from anthracite coal and pitch, has a much higher density (1·175), while the still less active carbon No. 3, with the low service time of 11 minutes, has a very high density (1·490) (all of these data refer to the lump density).

(To be continued).

## SOME REFLECTIONS ON LEAD ALLOYS.

M. LEON GUILLET observes that he made a profound study of lead-thallium alloys, and that the formation of the diagram revealed the following particulars.

The liquidus, and consequently the solidus, present a maximum corresponding to the combination $Pb_2Tl$, which enters into solution in lead.

Now hitherto the two following facts have been noted :—

1. A combination is hard and fragile.
2. When two metals enter into solution they are both malleable or both not so.

Lead and thallium being soft metals, and the combination entering into solution, it is evident that one of these two general principles must fail in the case in question.

Experience has demonstrated that it is the first which is wanting. There is a minimum hardness in the combination. The diameters of the impressions made in Brinell ball tests of pure and combined metals were :—

Pb : $d=3·95$. $Pb_2Tl$ : $d=4·30$ Tl : $d=4·05$.

A curious detail must be noted. It being very difficult to polish lead-thallium alloys, they were melted in crucibles with a polished aluminium-bronze bottom plate. If we add these results to the observations made by M. Nicolardot, viz., that these two metals do not harden at an ordinary temperature but at a very low one, a proof that their annealing temperature is below the ordinary one, we can see that there is a very interesting subject for study.—*Comptes Rendus*, October 15.

## INDIAN INDUSTRIES.

The first volume of the *Journal of Indian Industries and Labour** is now complete with the issue of part 4.

To this part of the Journal, Mr. B. Abdy Collins, Director of Industries, Bihar and Orissa, has contributed an interesting review of the industrial situation in Chota Nagpur and Orissa, touching on the natural resources of the tract, which "contains nearly all the coal and most of the iron ore hitherto located in India, besides other minerals such as copper, chromite, mica, limestone, manganese, monazite, graphite, bauxite, china clay and fire clay". The article includes a survey of the great metallurgical works already established, the schemes in hand for their development, and for the institution of new subsidiary industries. The author's views on the problems of the coal trade and railway transport will be of general interest, since the difficulties with which the industries of his province are faced in this respect are by no means confined to Bihar and Orissa.

Mr. Kale's article on the economic aspect of the boycott of foreign cloth provides much food for reflection. A stalwart apostle of the *swadeshi* principle, yet he calls attention to the danger of diverting labour from mills and factories to hand-spinning and hand-weaving The argument for the other side is expounded by Mr. K. Sanjiva Rao, Textile Expert to the Government of Bihar and Orissa, whose note on hand-loom weaving in India deprecates both on economic and on social grounds the strangling of that industry by factory development, and propounds a scheme for its revival even in the teeth of the large scale power-loom mills.

Much has been said and written in the past about the lack of manual skill displayed by the average Indian craftsman, and the crying need for providing facilities for his technical training. Those interested in the subject will do well to read Mr. Cove's article "Technical Training", in which he cites a number of trades, which are characterized by bad workmanship, due to lack of training. His criticisms are pungent, and it is possible that some of his cases may be overstated, but few will challenge his conclusions; coming moreover from a practical man who for many years has been in intimate contact with the class of labour which is the subject of his article, his remarks should no go unheeded.

Miss Broughton's article on the problem of

*Journal of Indian Industries and Labour*, Volume 1, Part 4, 158 pages, Calcutta. Superintendent, Government Printing, India. Price Rs. 4-8-0 per annual volume of 4 parts or Re. 1-8-0 per part, postage free

industrial fatigue in India deserves the attention of all who are in any degree responsible for the efficiency of factory administration and the well-being of factory labour. Her account of the effect on output caused by a shortening of the working hours in a well-known English factory will no longer come as a surprise to those who have studied the physiological side of labour; but many will be interested to hear how by a study of the movements involved in certain work, by training the workers, improving appliances and exacting shorter hours of work with higher wages, an iron foundry increased its weekly output from 3,000 plugs (the estimated capacity of the plant) to 20,000—while another firm, with larger plant, found it difficult to maintain an output of 5,000 plugs. A striking commentary on the practical effect of good ventilation in factories is to be found in the graph which accompanies Miss Broughton's article.

To those interested in tanstuffs, particularly in the exploration of new tanning materials Mr. Das's article "Mangrove swamps in the Sunderbans Forest Division, a valuable source of tanstuffs" will commend itself. The writer recapitulates the results of Mr. Pilgrim's investigation into the tanning qualities of various mangroves of these tracts, and gives in tabular form an account of the behaviour of the tanstuffs when utilized experimentally at the Calcutta Tanning Research Institute.

"The Bengal (Smoke) Commission had been so successful that in less than three years it had diminished the dense smoke from (Calcutta) factory chimneys by over 80 per cent." This statement, made in the House of Lords in 1914, speaks for the efficiency of the measures taken to reduce the smoke nuisance in Calcutta. Mr. Robson has contributed an article to the Journal in which he outlines the way in which the Smoke Commission grappled with the smoke nusiance in Calcutta; his remarks on the reduction of fuel-costs due to improved types of furnaces will repay reading. The general public too are interested in that smoke reduction and control means a considerable saving in the laundry bill.

Mr. Barbour, of the Titaghur Paper Mills, has contributed an article on modern paper-making, which will be read with interest by persons interested in forest exploitation and by paper manufacturers generally. He refers to the vicissitudes of the industry in the past, the difficulties that beset it at the present and the steps which he advocates to set it on a firm and permanent basis for the future.

The fourth part of the Journal contains also among other things a summary in tabular form of industrial disputes during the third quarter of the current year, summaries of "industrial intelligence" contributed by each province, miscellaneous notes (which include a note on briquetting experiments with Indian charcoal undertaken in the United States of America) and an abstract of the Bulletins of Indian Industries and Labour published during the year

Since the issue ofthe third part of the Journal the following bulletins have been published :—

No. 16.—Notes on Indian Piece Goods Trade.

No. 17.—The Genoa Labour Conference (official correspondence).

No. 18.—Proceedings of the third Conference of Departments of Industries held in Simla on the 23rd to 26th May, 1921.

## HIGH TAXATION.

### THE F.B.I. AND THE CHANCELLOR OF THE EXCHEQUER.

SIR,—I enclose copy of a letter which has been forwarded to-day to Sir Robert by Col. O. C Armstrong, the President of the Federation of British Industries.

The mass of evidence collected from the chief industrial centres of England, Scotland and Wales points to the fact that the present burden of taxation is crippling the efforts of manufacturers to recover and extend their foreign markets, and is stifling the possibility of a trade revival, which is so urgent if an alleviation of the present unemployment position is to be achieved.

The Federation feel it their duty to warn the Government of the certain consequences that will result if taxation on industry is maintained at its present high level, and is pressing the Chancellor of the Exchequer for a reduction of the Income Tax and the abolition of the Corporation Profits Tax.—I am, Sir, yours faithfully,

S. D. BENBOW HEBBERT,
Director's Department.

To The Rt. Hon. Sir ROBERT S. HORNE, C.B.E., K.C., M.P.

SIR.—The Federation of British Industries has just concluded its annual investigation into the effects of the past year's taxation, and the views of Industry as to the future. In the course of this investigation general meetings were held at Sheffield, Nottingham, Bristol, Swansea, Leicester Dundee, Edinburgh, Glasgow, Newcastle, Northampton, Birmingham, Liverpool, Manchester, Bradford and Leeds, at which unanimous resolutions in the most emphatic terms were passed demanding the abolition of the Corporation Profits Tax and an immediate and substantial reduction in the rate of the Income Tax.

The fall of prices and values during the past year has been unprecedented both in extent and rapidity, with the result that the effects of taxation have been felt by industry with peculiar severity.

The capital resources of many industries have already been strained to the utmost by the need for larger working capital to meet post war conditions of production, and the operations of Excess Profits Duty have prevented the accumulation of reserves sufficient to meet so serious a crisis, while enormous local taxation and the Corporation Profits Tax still further depleted the available resources of Industry during the year.

Under these circumstances the burden of Income Tax at a high rate, assessed upon the average of the three years which included the greatest industrial boom in history, has assumed crushing proportions, and many firms have already been driven to impair their future productive capacity by paying the current years' taxation out of

capital or by loan.

It is fully realised that high taxation has only been one among the many contributory causes of the present depression. It is, however, the only one of these causes which can be mitigated promptly by the independent action of His Majesty's Government.

The chaotic condition of the exchanges, the adverse financial and political conditions prevailing in many of our principal markets and the general disorganisation of the world's commercial system are all susceptible of remedy, but the remedy will take time, and most of these factors will still be in operation to restrict trade and hamper production during the forthcoming year.

Under these circumstances it was the unanimous opinion of the District General Meetings that any attempt to maintain taxation at its present level during the forthcoming year must at best seriously retard any industrial recovery, and at the worst may involve a permanent diminution in the productive capacity of the country.

The evidence brought forward at these meetings by speakers from all industries showed that the present rate of taxation is stifling initiative, postponing development, and crippling the efforts of manufacturers to recover and extend the foreign markets which are now of such vital importance to the welfare of the country.

The Federation warned the Government last year that Industry anticipated the most serious results from a continuance of high taxation. The meetings of this year afford overwhelming evidence that this warning was fully justified and have disclosed the gravest alarm as to the future if the present level of taxation is maintained.

The Federation desire to urge you most earnestly to consider the grave danger to the economic position of the country which will be involved by disregarding this warning a second time and to realise that the question is not now one of mere hardship or even of possible disaster to individual firms, but whether the whole industrial system of the country can possibly withstand any prolongation of the strain to which it has been subjected.

They feel that it is outside their province to suggest to you the means by which a sufficient reduction of taxation could be rendered possible They wish, however, to place on record their conviction that under the present circumstances Government activities must be reduced substantially below their pre-war level. They are fully aware that such a reduction will involve the sacrifice of many activities admirable in themselves and valuable to the country, but it is in their opinion better to face these sacrifices now when so doing may avert still more serious consequences, than to postpone them to a future date when the ruin of Industry and a dwindling revenue will force them upon the country.

They trust that the Committee which has been sitting under the Chairmanship of Sir Eric Geddes will be able to suggest to you economies sufficient to enable the necessary reduction in taxation to be effected immediately, since they are convinced that such a reduction would have a psychological effect both at home and abroad which would be of the utmost value at the present moment in restoring confidence and enterprise, and indeed might of itself alone provide a sufficient stimulus to start the revival of trade which is so urgently needed.

They are firmly convinced that a substantial reduction of taxation would in a short time so increase the general volume of trade as to yield a larger revenue than could possibly be hoped from its maintenance at a higher level.

The Federation feel that they would fail in their duty as the responsible and representative organisation of Industry in this country if they did not use their utmost endeavours to impress upon you and upon His Majesty's Government their firm conviction that any step, however bold, is preferable to the certain consequences of the maintenance of taxation at its present level.—I am, Sir, your obedient servant,

O. C. Armstrong, President.

## PROCEEDINGS OF SOCIETIES.

### SOCIETY OF GLASS TECHNOLOGY.

The Forty-Eighth General Meeting of the Society of Glass Technology was held in University College, London, on Wednesday, December 4, 1921, at 2.45 p.m., the President, Dr. Morris W. Travers, F.R.S., in the Chair.

During the forenoon, by the courtesy of the Directors, a party of some 60 members of the Society paid a visit to the Charlton works of Messrs. United Glass Bottle Manufacturers, Ltd.; lunch being also very kindly provided. Apart from the oil-fired furnaces, chief interest centred round the 10-arm Owen's automatic bottle-making machines, some of which were turning out nearly 60 bottles per minute.

At the afternoon meeting, the members expressed their cordial appreciation of the facilities accorded them in a hearty vote of thanks to Mr. G. E. Alexander, O.B.E., and his co-directors on the Board of Messrs. United Glass Bottle Manufacturers, Ltd.

The following papers were then given :—

"*A Suggested Method of Investigating the Viscosity of Glass.*" By I. Masson, N. F. Gilbert, and H. Buckley.

In presenting this paper, Mr. Gilbert observed that few methods were suitable. The one they had used was that of dropping a metal sphere, usually a ball-bearing, into a viscous substance such as syrup, and applying a modified form of Stokes' law. Ocular measurement of the rate of fall of the metal sphere agreed fairly well with the X-ray measurement where the shadow of the sphere was projected on to a photographic plate. In the case of molten glass, alundum crucibles had been found quite satisfactory, with platinum or large nickel balls. Lantern slides were shown in illustrating the method.

Dr. Masson having also spoken, the President Mr. F. Twyman, and V. H. Stott, took part in the discussion that followed.

"*Note on Pipettes.*" By Verney Stott, B.A. (National Physical Laboratory).

This paper was illustrated by lantern slides, the conclusion arrived at being: (*a*) Pipettes should

be adjusted for a particular delivery time, and when testing pipettes it is important to record both the delivery time and capacity; (*b*) the delivery time should be within certain limits as pipettes are unsatisfactory if the delivery time is too short, and also if it is too long; (*c*) a definite period should be allowed for drainage when graduating, testing, and using pipettes.

The PRESIDENT and Messrs. TOWERS and A. STEVENSON contributed to the discussion that followed.

*"The Annealing of Glassware and Annealing without Pyrometers."* By F. TWYMAN.

This paper, which was illustrated by lantern slides, experiments, and demonstrations, gave an account of some work done since the reading of a paper on "Annealing", before the Society in February, 1917. It was based on the assumption that so far as the practical annealing of glassware was concerned, the problem was simply one of the release of strain in a highly viscous liquid. There were two difficulties involved in determining the annealing temperature of a glass from its viscosity. The first is fundamental. If E is the modulus of elasticity, T the time of relaxation, then the viscosity is $E \times T$. But the time of relation cannot be determined from the viscosity unless at the same time the modulus of elasticity be known, and data are not available for the modulus of elasticity of glasses at temperatures within the annealing range. At the same time, glasses do not enormously vary their moduli of elasticity as the temperature is raised, and a very big change of modulus of elasticity would be necessary to cause any important difference of annealing temperature. The second objection is of a practical nature. In determinations of annealing temperatures which are obtained by means of measurement of viscosity, one requires to measure the temperature at which the viscosity of the given glass has an observed value. This requires a pyrometer, and a small easily controllable furnace.

The method proposed removes both these objections and is based on Maxwell's expression for the removal of strain in viscous solids. If we define the desired state of annealing by saying that we require the stresses originally present to be reduced in a particular proportion we may write as original stress $F_0$ and we then have the proportion of stress left in the glass at the end of time $t$.

$$\frac{F}{F_0} = e - \frac{t}{T}$$

T being the time of relaxation.

If now we can observe, during the process of annealing, the proportion of stress left in the glass (compared with that present before the process commenced) from time to time, we can stop the process when that proportion has arrived at a sufficiently small fraction, say 1/10 or 1/20, and nothing further is necessary. In stating the problem thus we no longer rely on Maxwell's law, but merely assume that $\frac{F}{F_0} = f(t)$ when $f(t)$ does not depend on the stress. Now, although we cannot conveniently observe the stress F on the objects themselves during annealing, we can do something nearly as good. A piece of the glass required to be annealed (which piece may be of any shape and size so long as it is possible to deform it elastically by a comfortably perceptible amount) is introduced into the furnace among the articles to be annealed. It is elastically strained by a definite amount, sufficient stress being brought to bear to deform it to that extent, and is in this way brought to an artificially unannealed state. Periodically the stress is removed, and it is allowed to spring back if it will to its original shape. As the temperature of furnace is raised, a time will come when the test piece does not spring back entirely, and from a record of the time during which the piece has been kept strained at a particular temperature and the extent to which it recovers its original position, it would be possible if desired, to calculate the time of relaxation at the temperature. But for practical purposes that is not necessary, for if it springs back on release by one-half its originally strained amount, we know that it has been half annealed; if to one-tenth it is 90 per cent annealed, and so on, and this time is quite independent of whether the lehr has been kept at constant temperature during the annealing or not. And if the test piece deliberately strained is thus annealed, then the other objects which have passed through the same temperature and were originally strained by want of annealing, will become annealed simultaneously to the same degree.

Several forms of apparatus derived from these considerations were described and demonstrated.

A discussion followed in which there took part the President, Prof. E. G. Coker, Messrs. E A. Coad-Pryor, V. H. Stott, and R. L. Frink.

## CORRESPONDENCE.

### LINE ENTITIES AND LINE DOMAINS.

*To the Editor of the Chemical News.*

SIR,—In my article in last week's issue I omitted to mention that in the equation $A - B = hv$, the letters A and B here stand for the energies of the "stationary" states, corresponding to the respective radii They should be designated $A_1$ and $B_1$ to distinguish these values from the radii.

Moreover, in view of the statement I made about the velocity of the planet Mercury, I should explain that the advance of the perihelion is not due entirely to a change in velocity. Eddington in his book "Time, Space and Matter", remarks on this point as follows: "It had already been recognised that the change of mass with velocity may cause an advance of perihelion; but owing to the ambiguity of Newton's law of gravitation the discussion was unsatisfactory. It was, however, clear that the effect was too small to account for the motion of perihelion being $\frac{1}{2}$ $v^2/c^2$, or at most $v^2/c^2$. Einstein's theory is the only one which gives the full amount 3 $v^2/c^2$." $c$ is the velocity of light and $v$ the velocity of the planet. "It was suggested by Lodge that this variation of mass with velocity might account for the whole motion of the orbit of Mercury, if account were taken of the sun's unknown absolute motion through the aether," but Eddington has pointed out that if this were so the other planets would

give observable effects, and these do not exist. In Einstein's theory the sun's gravitational field has to be taken specially into account, as well as the change in velocity.—I am, &c.,

F. H. LORING.

## NOTES.

BOILER WATER AND PURIFICATION.—The scale-producing substances are chiefly calcium and magnesium bicarbonates and calcium sulphate. Three periods can be distinguished in the formation of scale, viz: (1) precipitation of calcium carbonate; (2) that of magnesium carbonate (104°-115° C.); (3) precipitation of calcium sulphate at 140° C. When there is silica in the water, there is a deposit after the commencement of boiling, of calcium silicate in form of a hard layer similar to porcelain and highly insulating even when very thin. All methods of chemical purification remove a greater or less quantity of scale-producing matter, but not the gases. On the other hand, water purified by chemical agents has usually too great a percentage of alkalinity, and this causes foam, involving frequent purging. Thus it is necessary to free the water from gas, *e.g.*, by boiling. Water thus treated should be run directly into the boiler. If stored in tanks it should be kept out of contact with the atmosphere so as not to absorb oxygen or carbonic acid.—*Bull. Soc. Chimique*, October 20, 1921.

A NEW PROCESS FOR ESTIMATION OF SILICA.—Everyone is acquainted with the difficulties in quantitative analysis of silica, in presence of a *great excess of alkaline salts*. These difficulties were very carefully studied by Hildebrand, who demonstrated that in spite of two insolubilisations in a hydrochloric medium, all the silica was not obtained, and that the non-precipitate silica was not found quantitatively with the alumina in analysis. Substituting $HClSO_4H_2$ he attained more precise results. It was with a view to finding a less long process giving better results that M. Travers studied a method. He demonstrated that it enables a precise estimate of silica to be made, in presence both of fluorine and alumina, whereas Berzelius' method gives inferior results. This method is particularly interesting for in re search for $SiO_2$ in presence of fluorine. This separation is one of the most difficult known. The only methods described are based upon that of Berzelius, more or less modified. Finally, all the silica is obtained in one precipitation.—*Comptes Rendus*, October 24.

TEMPERATURE OF DRYING SAMPLES.—Some minerals and residues from various manufactures disengage even after complete dessication at 100° C., water in some cases and an oily volatile matter in others, when they are heated to 105°-110° C. Consequently different results are given when question of fixing the degree of humidity for the nett dry weight in the invoice, or the percentage of merchantable metal; *in dry matter* say contracts, but at what temperature? In some instances the percentages vary by several units, according to the temperature of dessication (water stove at 100° C. or hot air, 105°-110° C.). It cannot be denied that samples should be dried at the same temperature both for acceptance (nett dry weight) and analysis. It is to be desired that, by a generally admitted stipulation, a uniform temperature of 100° C. will be recognised, or in the absence of such agreement, that the temperature at which humidity has been estimated for delivery will be marked on the samples for analyses, thus avoiding disputes between the chemists of sellers and buyers or arbitrators.—*Annales de Chimie Analytique*, August 15, 1921.

SUGAR WORKS AMMONIA.—The Pithiviers Sugar Works (Soc. Sucrière de Pithiviers) intends to manufacture ammonia, for which purpose three processes have been acquired. The first and simplest consists in the recovery of nitrogen from beet which passes into the molasses and vinasse. Thus pure ammonia, acetic acid, and benzoic aldehyde are produced. Were all the molasses manufactured in France thus treated, 17,000 tons of sulphate of ammonia would be obtained .The other processes purchased by the company are synthetic. One is based upon the fixation of atmospheric nitrogen and subsequent decomposition of the compounds. The second is an elecric synthetic process yet being tested in the laboratory, but in a sufficiently advanced stage to be soon applied on an industrial scale. The first and second of these processes are shortly to be applied in this sugar works.—*L'Engrais*, Nov. 15.

ALSACE.—It is estimated that in 1922 the mines will produce 10,000 metric tons of potassium chloride, considerable quantities of which will be available for export.—*L'Engrais*, November 15.

NORWAY.—The shares of the Notodden Nitrogen Co. have risen in consequence of the Oppau catastrophe, a formidable riva lbeing thus removed. The Notodden and Rjnkan Works will now be enlarged and the workmen recently discharged given employment.—*L'Engrais.*

ECHO OF COAL STOPPAGE.—The disastrous policy of withdrawing the safety men from the mines during the coal stoppage of last Spring is in no small degree responsible for the high figure of unemployment among the workers of the mining industry. This is exemplified in the case of Hucknall No. 2 colliery, which has only just reopened since closing down on March 31 last Serious damage to the shaft resulted fom the total abandonment of the mine The management spared no effort to expedite the repairs necessary for re-opening the property, but this has proved a long and difficult business. There has been considerable distress among the workers formerly employed They have now been given the opportunity of signing on to re-start work.

£10,000,000 SAVED ON COAL BILL.—The Glasgow Chamber of Commerce, on December 12, in adopting a resolution demanding a reduction in Scottish railway rates, stated that the railway companies' expenditure had been decreased by £10,000,000 per annum owing to the reduced price of locomotive coal. A reduction in railway rates was essential for a revival of industry.

SOUTH AFRICAN PAPER-MAKING PROJECT.—A company is being formed in Natal to undertake the manufacture of wrapping paper from wattle wood and spent bark from the wattle extract mills, states the *South African Journal of Industries*,

A process is reported to have been discovered by which excellent wrapping paper can be made from these materials. It is proposed to make news print from wattle bark combined with tambuki grass later on, and also cardboard for the manufacture of fruit and egg boxes from spent bark.

WATER POWER RESOURCES IN SCOTLAND.—The broad results of the Committee's enquiries are as follows: They find that in Scotland, especially the Highlands, the natural conditions are such as to facilitate the production of power. In this area the bulk of the larger water-powers of the British Isles is situated, and although it is remote from the present industrial centres, no part of it is far from the sea or the Caledonian Canal. The larger water-powers of Wales are situated in the north-western portion of the Principality. As compared with the Scottish water-power resources, the cost of developing the larger of the Welsh resources as separate schemes would usually be high. While there are several schemes worthy of careful consideration on an individual basis, it would be desirable to consider the development of a number of the less favourable as adjuncts to other more favourable schemes. As in the case of Scotland, there are numerous sites capable of developing small blocks of power. As regards England, generally, the main sources of water-power are the small falls on rivers. The Committee consider, however, that the aggregate output from these sources could be materially augmented by installing modern plant, replanning existing sites, and generally improving the water-courses. In Ireland a certain amount of power can be developed from high level lakes in the mountainous areas, but the main sources of water power are to be found in the rivers. It is generally considered that the utilisation of the water powers of the United Kingdom would tend to relieve the increasing congestion of our large centres of population, and in the case of the Highlands of Scotland would assist materially in improving the present low standard of comfort of the inhabitants of that area, and thus arresting the abnormal emigration from it. The potential water power of the schemes before the Committee (not the total available) was estimated at 194,965 kilowatts (continuous) in Scotland, 35,900 kilowatts in Wales, and 20,440 kilowatts in England. The Irish Sub-Committee made an estimate of 280,000 kilowatts (continuous) as the total available potential water-power in Ireland It was further estimated for Great Britain that probably 210,000 kilowatts (continuous) could be developed at an economic rate. This was given as the equivalent in energy of nearly three million tons of coal per annum burnt in steam plants.—*Board of Trade Journal.*

TOKIO PEACE EXHIBITION.—The Department of Overseas Trade is in receipt of information regarding the forthcoming Peace Exhibition which is to be held there from March 10 to July 31, 1922. It would appear that all the space available for foreign exhibits has been over applied for. Messrs. Arthur Buckney & Co., of Tokio, have, however, secured a special site for the erection of a British Pavilion, and intending exhibitors can obtain space therein on application to the London office of the firm at 40, Westminster Palace Gardens, Victoria Street, S.W.1. Rebates of freights on goods for exhibition have been arranged by Messrs. Buckney, ranging from 20 to 50 per cent, according to date of shipment Intending exhibitors should lose no time in communicating with Messrs. Buckney, who are prepared to arrange all details, supply attendant staff at Tokio, and safeguard exhibitors' interests in every possible way.

## New Patents.

THIS List is specially compiled for the *Chemical News* by Messrs Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, W.C.2, from whom all information relating to Patents, Trade Marks and Designs can be obtained gratuitously.

*Latest Patent Applications.*

32859—Bichowsky, F.—Processes of producing [illegible] nitrogen compounds. December 7.

*Abstract Published this Week*

*Ammonium Sulphate.*—Patent No. 170613.—Some improvements in processes for the production of Ammonium Sulphate have been invented and Patented by Mr. P Parrish of The South Metropolitan Gas Co., 709, Old Kent Road, London In the production of ammonium sulphate by passing into a saturator gases which are liable to contain cyanogen compounds, the cyanogen compounds are prevented from reaching the saturator by adding to the ammonical liquor to be distilled a polysulphide, or forming a polysulphide in the liquor, for instance by adding sulphur or blowing in air, so as to fix the cyanogen compounds in the liquor as sulphocyanides; or the vapour from the still may be passed over spent oxide on its way to the saturator. In the case of the direct process, the ammonical gas is passed through a washer containing a polysulphide solution.

Messrs. Rayner & Co., will obtain printed copies of the published specifications and will forward on post free for the official price of 1/- each.

## NOTICES.

**EDITORIAL.**—All Literary communications and Books, Chemical Apparatus, &c., for review or notice to be addressed to the EDITOR.

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